PB82-239286

Feasibility of Developing a Comprehensive Methodology for Source Identification and Environmental Loading (Materials Balance)

Arthur D. Little, Inc.
Cambridge, MA

Prepared for

Environmental Research Lab.
Athens GA

Apr 82

U.S. Department of Commerce
National Technical Information Service
NTIS

PB82-239286

EPA 600/3-82-047

FEASIBILITY OF DEVELOPING A COMPREHENSIVE METHODOLOGY FOR SOURCE IDENTIFICATION AND ENVIRONMENTAL LOADING (MATERIALS BALANCE)

by

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TYPING GUIDE SHEET

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-600/3-82-047

2.
ORD Report

3. RECIPIENT'S ACCESSION NO.
PB82-239286

4. TITLE AND SUBTITLE
Feasibility of Developing a Comprehensive Methodology for Source Identification and Environmental Loading (Materials Balance)

5. REPORT DATE
April 1982

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
A.E. Wechsler, A.Q. Eschenroeder, D. Gilbert, K. Loos, P. Poston, and J.M. Stevens

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Arthur D. Little, Inc.
Cambridge, Massachusetts 02140

10. PROGRAM ELEMENT NO.
ACUL1A

11. CONTRACT/GRANT NO.
68013857

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Research Laboratory--Athens GA
Office of Research and Development
U.S. Environmental Protection Agency
Athens, Georgia 30613

13. TYPE OF REPORT AND PERIOD COVERED
Final, 4/79-8/79

14. SPONSORING AGENCY CODE
EPA/600/01

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A materials balance is an array of the flows of materials or chemicals from the cultural environment to the first point of entry into the natural environment and includes information regarding the location, time rate, quantity and chemistry of the inflows. The materials balance encompasses two major components--identification of sources and materials and estimates of environmental loadings. The scope and focus of a materials balance is determined by various characteristics, such as geographic scale, time frame, environmental media or chemical class.

Feasibility criteria are presented to evaluate the various approaches. The feasibility criteria are degree of uncertainty in source or quantities, human resource requirements, time constraints, identification of controllable sources, applicability to exposure predictions, comprehensiveness of the method, ability to use similar chemicals as guides, interfacing with fate models, accuracy of results, compatibility with existing data, applicability of method to different geographic scales, resolution of results in time and space, requirements for monitoring data, use of confidential information, data processing demands and complexity of input data and method.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS *(This Report)*
UNCLASSIFIED

20. SECURITY CLASS *(This page)*
UNCLASSIFIED

21. NO. OF PAGES
107

22. PRICE

EPA Form 2220-1 (9-73)

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FOREWORD

As environmental controls become more costly to implement and the penalties of judgment errors become more severe, environmental quality management requires more efficient management tools based on a greater knowledge of the environmental phenomena to be managed. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, The Technology Development and Applications Branch develops management or engineering tools to help pollution control officials achieve water quality goals through watershed management.

A comprehensive materials balance methodology that can be applied to a variety of toxic or hazardous pollutants is needed in the development of environmental fate models and risk assessment techniques. In developing a materials balance methodology, all processes that result in environmental loading--manufacture, processing, transportation, storage, disposal, and others--need to be considered. This report describes a study to examine the overall feasibility of a systematic approach to source identification and environmental loading estimation and to outline the most feasible materials balance methods.

David W. Duttweiler
Director
Environmental Research Laboratory
Athens, Georgia

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ABSTRACT

A materials balance is defined as an array of the flows of materials or chemicals from the cultural environment to the first point of entry into the natural environment and includes information regarding location, time rate, quantity and chemistry of the flows. The materials balance encompasses two major components--identification of sources of materials and estimates of environmental loadings. The scope and focus of a materials balance is determined by various characteristics, such as geographic scale, time frame, environmental media or chemical class.

The materials balance framework depicts the interrelationships of controlled and accidental flows of the material in various industrial, commercial and consumer activities. The activities considered are extraction, refining, manufacturing, processing, transportation, storage, use and disposal; natural sources are also included. Air, land and water represent the environmental compartments receiving the pollutant loading. A general and specific approach to each activity is described. A checklist is presented to assure completeness in performing the materials balance. The checklist is a matrix comprised of sources (activities) and environmental inputs (flows).

Feasibility criteria are presented to evaluate the various approaches. The feasibility criteria are degree of uncertainty in source or quantities, human resource requirements, time constraints, identification of controllable sources, applicability to exposure predictions, comprehensiveness of the method, ability to use similar chemicals as guides, interfacing with fate models, accuracy of results, compatibility with existing data, applicability of method to different geographic scales, resolution of results in time and space, requirements for monitoring data, use of confidential information, data processing demands and complexity of input data and method.

The report was submitted in partial fulfillment of Contract No. 68-01-3857 by Arthur D. Little, Inc., under the sponsorship of the U.S. Environmental Protection Agency. The report covers a period from April 1979 to August 1979, and work was completed as of November 1979.

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ACKNOWLEDGEMENTS

Arthur D. Little, Inc., staff contributing to this task included: Alan Eschenroeder, Diane Gilbert, Karl Loos, Paul Poston, Janet Stevens and Alfred Wechsler. The authors are appreciative of the assistance, suggestions, and guidance provided throughout the conduct of this task by Dr. James W. Falco, Office of Research and Development, Environmental Research Laboratory at Georgia; Mr. Mark Segal and Mr. Richard Seraydarian Monitoring and Data Support Division, Office of Water Planning and Standards, Washington, D.C.; and Dr. Richard Cothern, Office of Toxic Substances, Washington, D.C.

SECTION 1

INTRODUCTION

BACKGROUND

The Office of Research and Development, Environmental Research Laboratory, Athens, Georgia, has requirements for materials balances as inputs to environmental fate modeling efforts and in research on the distribution and disposition of environmental pollutants. The Monitoring and Data Support Division, Office of Water Planning and Standards of the U.S. Environmental Protection Agency is currently conducting a program to evaluate the exposure to and risk from the presence of toxic pollutants in the nation's environment. As part of this program, there is a requirement for the development of a comprehensive and systematic methodology for materials balances to be used in exposure and risk assessment. The EPA Office of Toxic Substances also has requirements for materials balances for use in risk assessments of chemicals prior to their production and use as well as in examining existing chemicals which may have potential harmful effects on man and the environment. Thus these three offices share a common requirement for a comprehensive materials balance methodology which can be applied to a variety of toxic or hazardous pollutants.

Materials balances have several important uses: to predict exposure in the absence of monitoring data, to enable confirmation and/or extension of limited monitoring data, and to permit identification of critical controllable pollutant sources as part of risk abatement. Because of the limited coverage, high cost and extensive time requirements for monitoring studies, materials balances may be the most cost effective method of providing data for estimating exposure. Materials balances, in some cases, may be the only technique available to examine the contribution of a specific source to the ultimate risk of a pollutant. Therefore, a comprehensive and systematic methodology for materials balances--source identification and loading estimation--is a valuable part of a toxic pollutant regulatory program.

The two major elements of materials balances are source identification and loading estimation. It is important to consider and identify all major sources--natural and anthropogenic, deliberate and inadvertent--that can lead to potential exposure of humans and other biota including a characterization of the chemical or physical form in which the materials are released. All processes which result in environmental loading--manufacture, processing, transportation, storage, disposal and others--need to be considered. Furthermore, it is necessary to quantify the magnitude, location, and time dependence of the environmental loading since these factors form the basis for fate calculations, subsequent concentration determinations and exposure estimates. In the context of this study, however, the endpoint of the materials balance is the identification of sources and quantification of loadings to the "initial environmental compartments," e.g., the air, water, soil in which the release first occurs. Methods for establishing environmental fate and estimating exposure are not included in the materials balance methodology although the methodology must yield results that are compatible with the requirements of the environmental fate, exposure and risk assessment methodologies.

Several materials balance studies or approaches have been developed in the past for specific applications. The methods used have not been reviewed, analyzed, summarized, or generalized to the point where a comprehensive approach--suitable for many types of anticipated applications--is available. Furthermore, the feasibility and expected results of and resources required for materials balances have not been established.

STUDY OBJECTIVES

The objectives of this study are to examine the overall feasibility of a systematic approach to source identification and environmental loading estimation--materials balance--and to outline the most feasible materials balance method(s) and steps needed for implementation, so that they can be further developed and used in regulatory development by EPA.

APPROACH

As originally planned, the study was to include four major elements:

1. Develop criteria for assessing the feasibility of conducting materials balances for toxic pollutants and develop a scheme for using these criteria for ranking the feasibility of materials balance methods, particularly for new and existing chemicals.

2. Identify and examine available materials balance methods and select the best method(s) using the criteria identified in the first step.

3. Evaluate the use of a "checklist" or "matrix" approach for the organization, conduct and presentations of a materials balance.

4. Rank and critique the materials balance methods examined in terms of utility for regulation, flexibility for multiple use, needed resources, and limitations.

The first step was completed without difficulty. Feasibility criteria were identified and reviewed with EPA. An approach to using the criteria in ranking materials balance methods was then developed. After conducting a systematic and comprehensive literature search, and after reviewing materials balance reports, however, we concluded that: (1) few materials balance methodologies have been developed, (2) these materials balance methodologies were neither sufficiently comprehensive nor flexible enough to include the variety of sources or chemicals under consideration in this work, and (3) it would not be practical or useful to apply feasibility criteria or rank these existing materials balance methods.

As a result, our approach was restructured into the following work elements:

- First, a simplified framework for the conduct of materials balances was developed that included a broad range of industrial and consumer activities from raw material extraction through product disposal sources of environmental loadings--and that could account for routine, planned, fugitive, or accidental environmental releases.

- Second, new materials balance methodologies were developed for each of these industrial/consumer activities, incorporating existing approaches where possible. The methodologies were described in sufficient detail to show how the materials balance should be conducted, giving sample calculations and references to data and information that could be used in a materials balance; however, preparation of a step by step or "cookbook" method was not considered appropriate. In describing the use and applicability of the materials balance methods the feasibility criteria identified earlier were considered.

- Third, an expansion of the checklist or matrix approach to organizing and presenting the results of a materials balance was examined.

The results of these three work elements, combined with the feasibility criteria, provide the EPA with a comprehensive framework and approach to the conduct of materials balance suitable for regulatory development in support of water pollution and toxic substance control programs.

REPORT ORGANIZATION

Section 3 presents the overall framework for materials balances. Section 4 presents the materials balance approaches appropriate for the following activities: extraction, refining, manufacturing, processing, transportation, storage, use, and disposal. In addition to these activities, we have included a discussion of natural sources. Section 5 presents a brief discussion of the checklist/matrix approach. In Section 6, the criteria for evaluation of feasibility of materials balance are presented, and a general discussion of the materials balance methods in light of these criteria is given. An annotated bibliography of pertinent reports and articles on materials balances is given in the Appendix.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Materials balances provide useful data for exposure and risk assessments, environmental fate modeling, evaluations required as part of the Toxic Substances Control Act and research on the distribution and disposition of pollutants in the environment. A number of materials balances have been performed and reported in the literature; most of these materials balances are limited or restricted. Some consider only certain geographic regions whereas others deal with only a limited number of industrial or consumer activities that may produce pollutants. Also a specific methodology for performing materials balances has not been developed.

A materials balance methodology should be complete in its coverage and adaptable to each particular case of interest. A variety of factors determine the usefulness and compatibility of a methodology with a particular materials balance program. These factors have been summarized in feasibility criteria developed as part of this task. A methodology is outlined for performing materials balances. In addition, a checklist has been developed to assure that all potential sources and sinks have been evaluated in performing the balance.

A complete materials balance must cover all activities in which a material participates from the point at which it enters the cultural environment until it returns to the natural environment. The activities may include extraction, refining, manufacturing, processing, transportation, storage, use and disposal. For completeness one should also consider natural sources of the material. Each of these activities must be examined in terms of inputs and outputs to the natural environment and to other activities. Although the general concept is the same for each activity, a different approach may be required for each specific activity.

The actual method selected for a materials balance will depend on a number of factors. The time and resources available for the project determine whether a thoroughly documented evaluation or only estimates will be accomplished. The scope of the study, in terms of time period covered, geographic area considered and activities evaluated, influences selection of the methodology. The specific material considered and availability of pertinent data determine whether sufficient factual information exist, whether estimates must be made, or whether analogies to similar chemicals will suffice. The desired output and use of the materials balance is very important in selecting a methodology. A study for use in risk assessment would require a different orientation and outputs from one to provide input to fate modeling. Each user must select those parts of the methodology that best fit the needs of the particular project.

The methodology and feasibility criteria presented in the report have not been applied in their entirety to a materials balance. The methodology is, in some cases, based on previous work but much of it represents the approach that the authors would suggest in performing a materials balance. Thus, a major recommendation from the conclusion of this work is that the methodology and criteria be tested in performing one or more comprehensive materials balances. This work would evaluate the usefulness and applicability of the methods, the feasibility criteria and the checklist as well as providing valuable input for modification and revision of the methodology to make it as useful as possible. A more detailed step-by-step procedure could be developed as part of the documentation of this work. In addition, the materials balance, per se, would provide important data for use in other EPA projects.

SECTION 3

FRAMEWORK FOR PERFORMING A MATERIALS BALANCE/SOURCE IDENTIFICATION

DEVELOPING A MATERIALS BALANCE FRAMEWORK

A materials balance may be defined as an array of flows of materials between two locations or compartments. These locations are determined by the needs of the person conducting the materials balance. Thus, the building engineer who is measuring the flow of air into a specific office within a building is conducting a materials balance as is the businessman who is measuring the flow of crude oil products between countries on a global basis. In either case, one of the keys to developing a materials balance is to carefully define the boundaries across which the materials will flow. These boundaries must be defined so that they are both mutually exclusive and all inclusive. In its simplest form, therefore, a materials balance might be completely described as shown in Figure 1.

While a materials balance is generally thought of as flows crossing geographic boundaries, it can be defined in terms of timing, products, processes, sources and uses, or cultures. Whatever the case may be, the more specific one can be in defining the needs and uses of a materials balance, the easier it will be to perform the analysis.

Since the purpose of developing this methodology is to be able to identify and quantify flows of chemicals and products containing chemicals into environmental compartments, it makes sense to describe the two environments as natural and cultural. The term "cultural environment" is defined here as all anthropogenic sources and activities. Since the natural environment is all encompassing, the relationship of these two environments is as shown in Figure 2.

Materials generally enter the cultural environment from the natural environment. Within the cultural environment, the materials are processed, used, disposed of, and eventually returned to the natural environment. If "coal used for electric power generation" were selected as an example, its relationship to the natural and cultural environment would be as shown in Figure 3. While this example is greatly oversimplified, it will be used to outline the development of a materials balance methodology.

Coal is generally thought of as being consumed in the cultural environment. However, it is merely its form that is being altered. Coal is extracted from the earth and enters the cultural environment as a solid material with high carbon content. It is transported, stored, sometimes processed (e.g., washed, crushed, etc.), and eventually burned to produce heat for steam generation to produce electric power. However, in addition

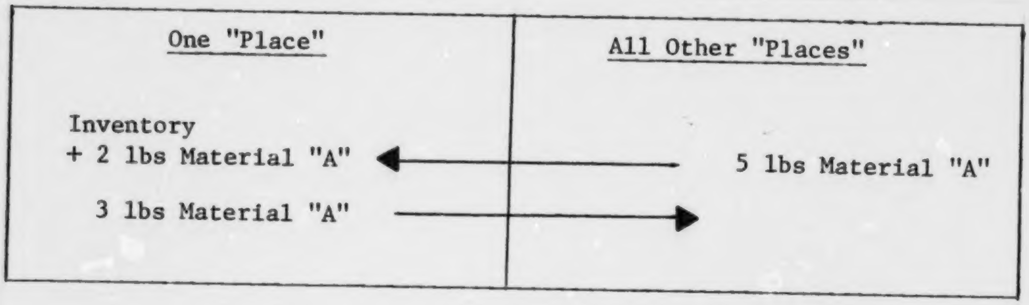
One "Place"
All Other "Places"
Inventory
+ 2 lbs Material "A"
5 lbs Material "A"
3 lbs Material "A"

Figure 1. Simplistic materials balance.

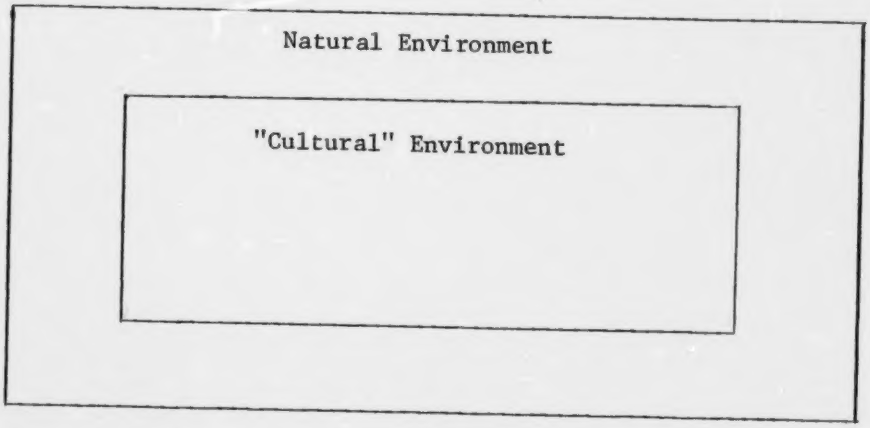
Natural Environment
"Cultural" Environment

Figure 2. Relationship of cultural environment to natural environment.

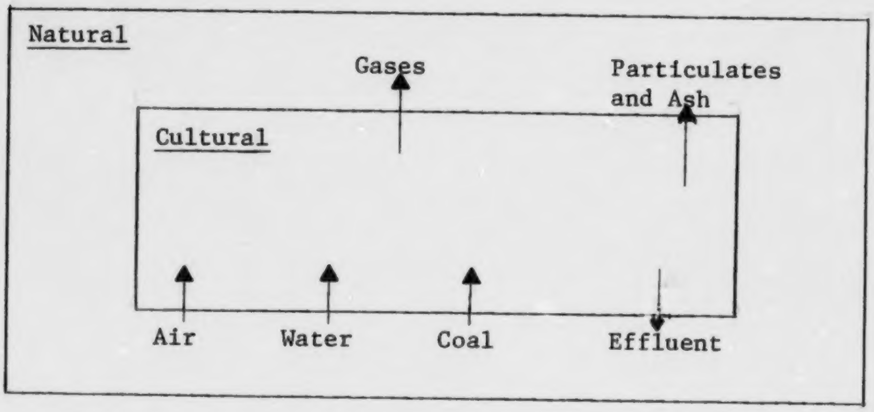
Natural
Gases
Particulates and Ash
Cultural
Air
Water
Coal
Effluent

Figure 3. Simplified materials balance using coal for electric power generation as an example.

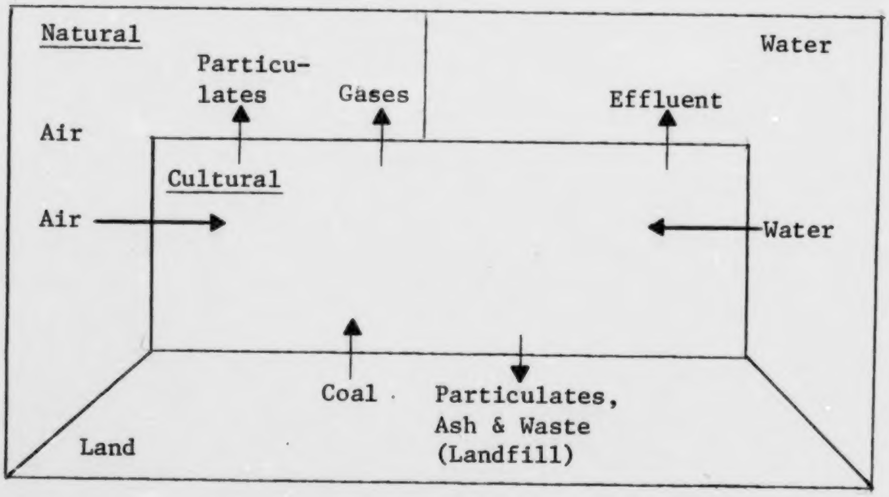
Natural
Particu-lates
Gases
Water
Effluent
Air
Cultural
Air
Water
Coal
Particulates, Ash & Waste (Landfill)
Land

Figure 4. Example of a material balance for coal, indicating environmental compartments.

to heat, combustion also produces gases, e.g., carbon monoxide, carbon dioxide, sulfur and nitrogen oxides, as well as particulates and ash. These "products" do not stay in the cultural environment but move back to the natural environment. This brings us to the concept of the environmental compartments: air, water and land. These compartments can be superimposed on the example for coal and show that, while some of the coal returns to the land compartment, a large majority enters the air in the form of gases. Figure 4 details these flows. While food may be considered as an individual environmental compartment, it is a specialized case and will not be considered in the development of this general methodology.

To complete the materials balance, it would be useful to define the pathways for product flows within the cultural environment. These pathways together with the environmental compartments can be used to identify both the sources and uses of chemical products crossing environmental boundaries. The pathways for the coal example are shown in Figure 5.

The basic framework for performing a materials balance using the coal example is now completed. Actually, several materials balances are defined in Figure 5. The first is the flow of material along the principal use route from extraction, storage, transportation, combustion and eventual disposal. This might be called the controlled or normal flow of materials that would be expected when one considers the combustion of coal. Another materials balance is comprised of the secondary flow of materials across environmental boundaries. These include several normal or controlled flows of materials, such as stack emissions to the atmosphere, as well as several uncontrolled or uncontrollable flows resulting from each of the identified activities. Specifically, these might include spills, exposure of miners to coal dust, leaching of materials from the soil in the landfill or unexpected particulate or ash emissions during the start up of a power plant. Therefore, one very important use of this diagram is the identification of likely uncontrolled emissions into either the cultural or natural environment.

The development of this methodology focuses on flows between the cultural and natural environment and not on flows between compartments in the natural environment. These particular flows are more properly treated in a fate and distribution analysis.

A more generalized materials balance flow diagram is shown in Figure 6. This diagram provides the basic framework for conducting a materials balance across environmental boundaries. The flow pattern shown in the diagram describes the normal or expected flows that one would consider when describing a product's life cycle. These are the normal transportation, use, and disposal streams that people would generally monitor, or at least be aware of. However, as previously cited for the coal example, many undefined, uncontrolled, uncontrollable, or unknown streams need to be considered when developing a materials balance flow diagram. It is the identification of these streams that will provide the most useful information to persons using this materials balance flow diagram. Several of the more basic uncontrolled flows are detailed in Figure 7.

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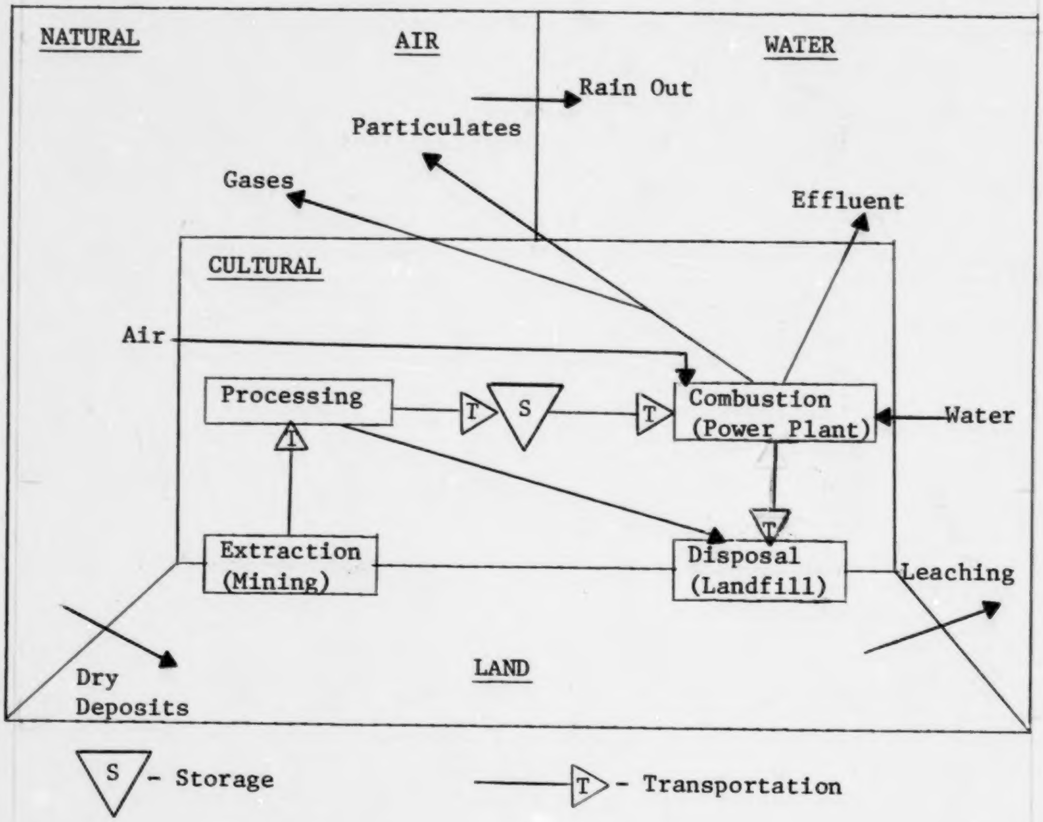
NATURAL
AIR
WATER
Rain Out
Particulates
Gases
Effluent
CULTURAL
Air
Processing
T
S
T
Combustion (Power Plant)
Water
T
T
Extraction (Mining)
Disposal (Landfill)
Leaching
Dry Deposits
LAND
S - Storage
T - Transportation

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Figure 5. Materials balance for coal detailing environmental compartments and pathways.

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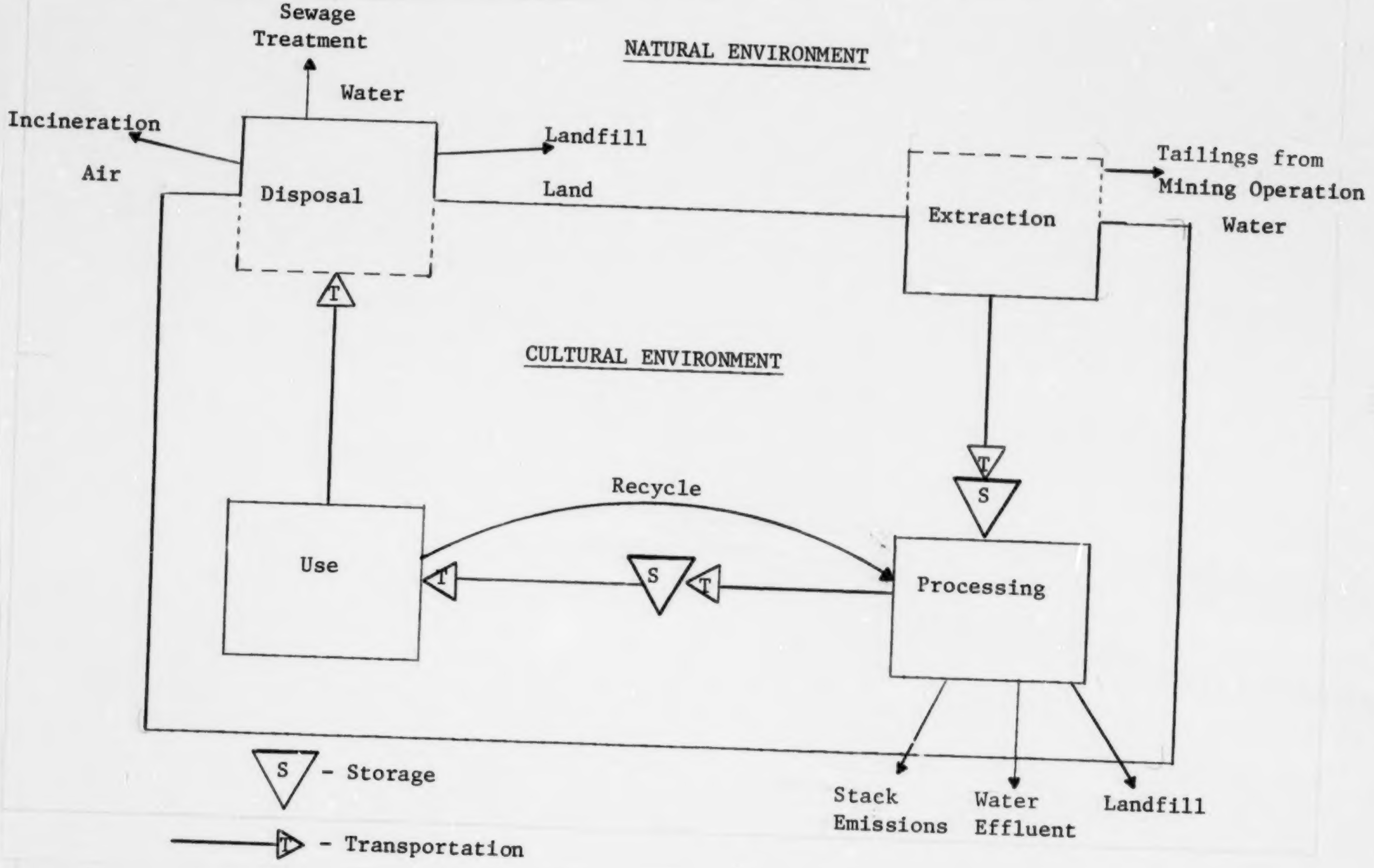
Sewage
Treatment
Water
NATURAL ENVIRONMENT
Incineration
Air
Disposal
Landfill
Land
Tailings from
Mining Operation
Water
Extraction
T
CULTURAL ENVIRONMENT
Recycle
T
S
Use
T
S
T
Processing
Stack
Emissions
Water
Effluent
Landfill
S - Storage
T - Transportation

Figure 6. Generalized materials balance flow diagram detailing an example of controlled emissions.

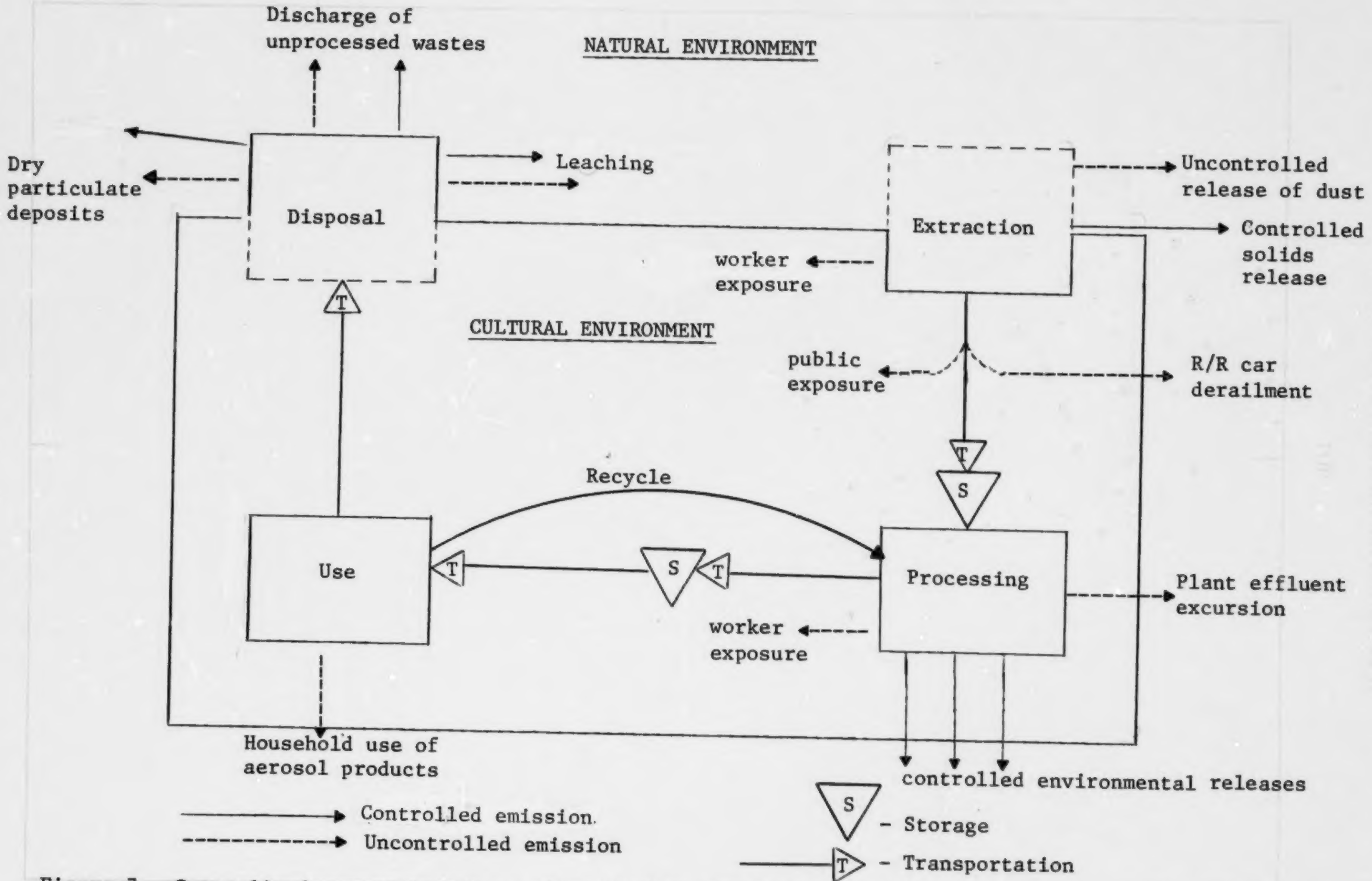
Discharge of unprocessed wastes
NATURAL ENVIRONMENT
Dry particulate deposits
Disposal
Leaching
Extraction
Uncontrolled release of dust
Controlled solids release
worker exposure
CULTURAL ENVIRONMENT
T
public exposure
R/R car derailment
T
S
Recycle
Use
T
S
T
Processing
Plant effluent excursion
worker exposure
Household use of aerosol products
controlled environmental releases
Controlled emission
Uncontrolled emission
S
- Storage
T
- Transportation

Figure 7. Generalized materials balance flow diagram detailing selected examples of uncontrolled flows.

Although not always the case, the controlled and known streams for any process generally represent less of an environmental threat than the unknown or uncontrolled flows. Even plant effluent streams may be considered "safe" if they are properly controlled and monitored. Should there be an excursion at this point, it would be well documented so that precautionary measures could be taken (to some extent, the plant effluent excursion is an uncontrolled flow and could be diagrammed as such). Using historical data, these flows can be thought of as vectors with the length corresponding to the quantity likely to be released at a specific point. In addition to being concerned about the quantity of the release, some thought should be given to the measure of human or biotic exposure at the point of release. Thus, each vector in the diagram can be accompanied by a parallel vector measuring the level of environmental exposure/risk. Such a generalized diagram is shown in Figure 8.

USING THE MATERIALS BALANCE FLOW DIAGRAM

What we have done so far is to develop a framework for performing a materials balance. We have not yet determined why or how a materials balance is going to be used. These are very important questions and need to be answered before gathering data or performing the analysis. Several important questions are:

- Who will use the materials balance flow diagram?
- What questions must it be able to answer?
- How well adapted is the materials balance to its intended application?
- What are the constraints for conducting the materials balance?

These and other questions are addressed in the general stepwise approach to conducting a materials balance shown in Figure 9. These steps detail the process for conducting an analysis and include specific informational and definitional needs required before proceeding with the analysis.

In step one, a first cut at the materials balance is made using the generalized framework described previously. This framework should be used to "make sense" of the chemical flows using whatever knowledge of the industry or chemical pathways is immediately available. This will provide a starting point from which to ask questions in order to better define the needs for a particular balance. In the second step, the scope of the analysis required and the intended approach are specified through a series of questions which focus the materials balance in a particular area. Because each materials balance is unique to the product, pathway, industry, geographic region or environmental compartment being studied, it is extremely important to devote sufficient time to this step in order to map out the analytical process. Although not intended to be an all inclusive list, many of the questions that need to be addressed are shown in Table 1.

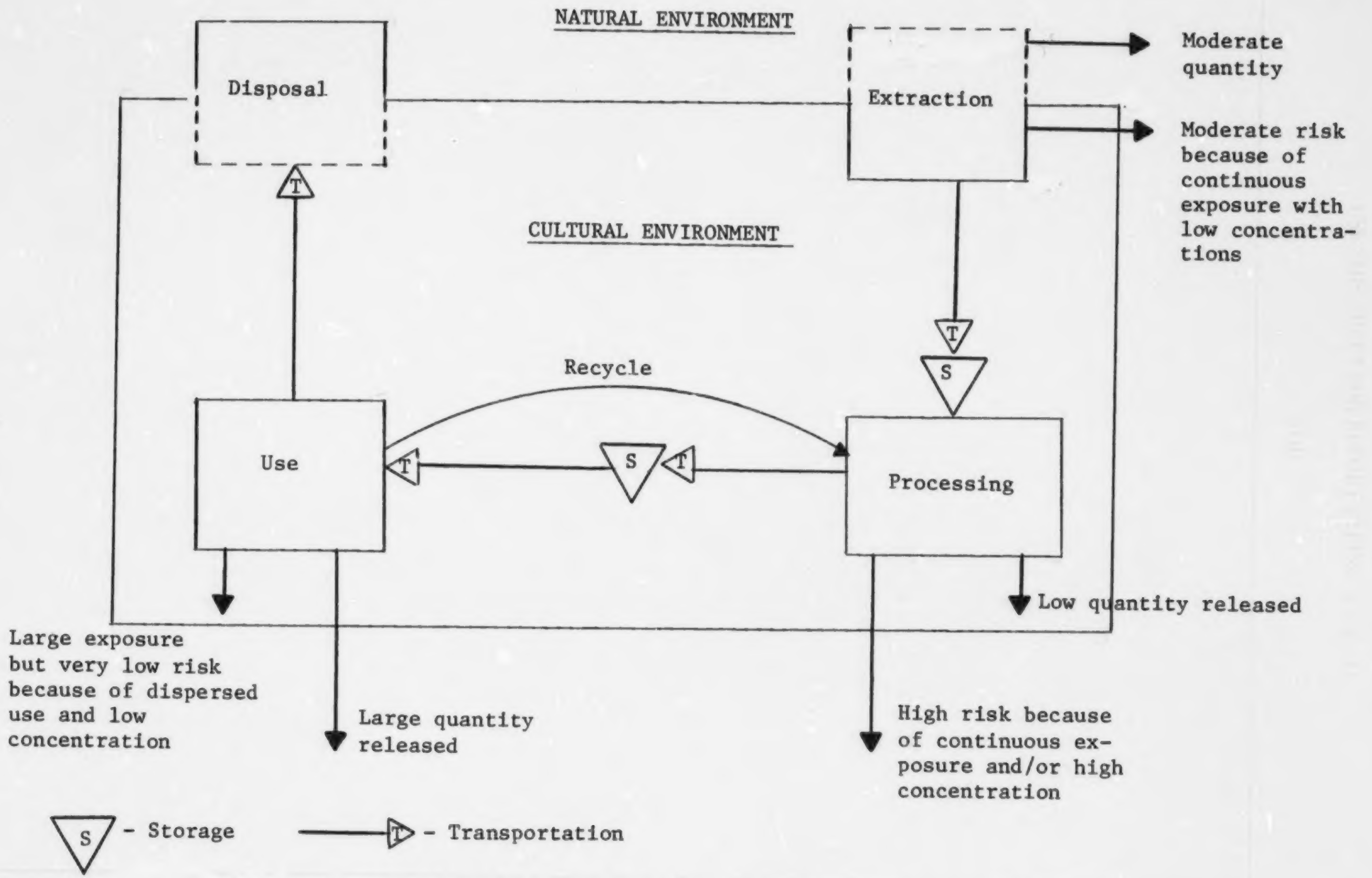
NATURAL ENVIRONMENT
CULTURAL ENVIRONMENT
Disposal
Extraction
Use
Processing
Recycle
T
S
Moderate quantity
Moderate risk because of continuous exposure with low concentrations
Low quantity released
Large exposure but very low risk because of dispersed use and low concentration
Large quantity released
High risk because of continuous exposure and/or high concentration
S - Storage
T - Transportation

Figure 8. Generalized materials balance flow diagram detailing vectors for quantity and exposure risk.

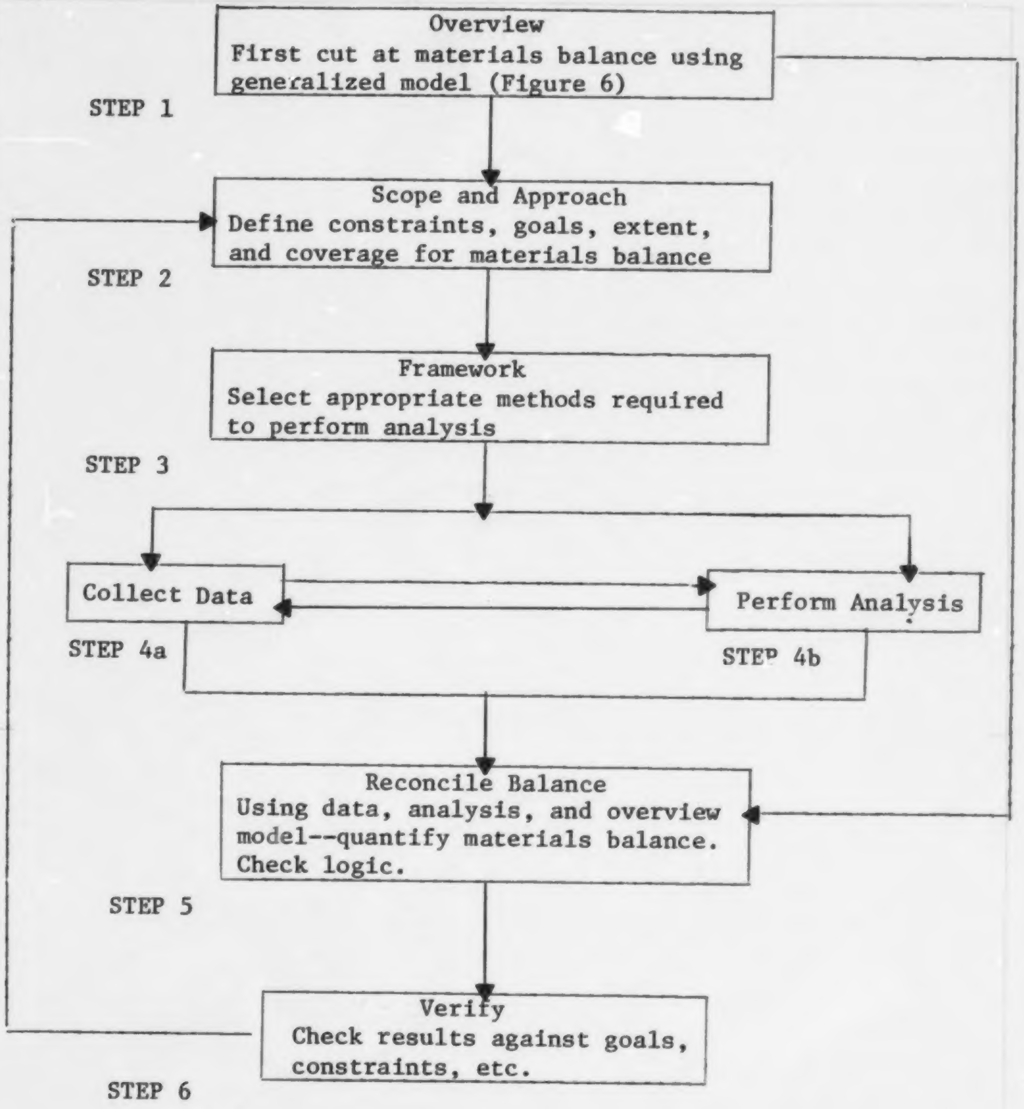
Overview
First cut at materials balance using generalized model (Figure 6)
STEP 1
Scope and Approach
Define constraints, goals, extent, and coverage for materials balance
STEP 2
Framework
Select appropriate methods required to perform analysis
STEP 3
Collect Data
STEP 4a
Perform Analysis
STEP 4b
Reconcile Balance
Using data, analysis, and overview model--quantify materials balance. Check logic.
STEP 5
Verify
Check results against goals, constraints, etc.
STEP 6

Figure 9. Flow diagram for performing materials balance.

TABLE 1. SCOPE AND APPROACH

1. What are time constraints?	• days • weeks-months • years
2. What is the extent of coverage desired?	• national baseline • community • regional
3. What basic approach is to be used?	• environmental compartments • pathways to the environment • product specific
4. What is focus (or goal)?	• identify high exposure/risk areas • identify large source processes • compare natural v. man-made sources
5. What level of detail required?	• broad, general level only "major" sources and uses • quantitative based on available information • quantitative based on sampling
6. What will material balance be used for?	• preliminary check on new chemicals under PMN • other government agencies (OSHA, EPA) • private business
7. How will results be displayed?	• quantity of material transferred to compartments • concentration/level of release • location of initial entry to compartments • rate of transfer to compartments
8. What analytical approach will be used?	• estimate losses from total production • estimate residual in environment directly • estimate natural/cultural totals • estimate accumulation of individual products
9. What activities will be studied?	• extraction • refining • manufacturing/processing • transportation/storage • use • disposal

In the third step, a detailed framework for conducting the analysis is prepared. Using the answers to questions from step two, the appropriate data requirements can be determined as well as the relevant industry segments, geographic areas, and environmental compartments which will be integral to this analysis. Each methodology consists of a general approach to the activity as it is applicable to each environmental compartment, references to the literature, a table or other example of the output, and a flow chart detailing the development of a materials balance for that activity. In a sense, this allows the person conducting a materials balance to customize the framework to the specific needs defined in step two.

Steps 4a and b provide for data collection and analysis. This is actually an iterative process whereby the data sources are developed as the need exists to provide more information to the analysis. Finally, in step five, the analytical results are summarized on the materials balance flow diagram and the data reconciled to eliminate inconsistencies and note any omission. At this time, the analyst may wish to return to the data collection and analysis steps to check the model for accuracy and completeness. This can be done by testing the model using known data. Finally, in step six, the completed methodology should be checked against the scope and approach defined in step two. The purpose of this step is to verify that all questions intended to be addressed have been addressed and that there are no gaps remaining in the analysis.

SECTION 4

MATERIALS BALANCE METHODOLOGIES

EXTRACTION ACTIVITIES

General Approach

Extraction is the first step in most materials balances, especially those involving minerals, coal, oil or natural gas. This step is limited to removing the material of interest from its natural depository in preparation for refining, manufacturing, processing, etc. The objectives of the extraction materials balance are to identify the location of the releases to the environment (i.e., in terms of the techniques utilized, actual location of the operation, etc.), the quantity and form of these releases and the amount available for transportation to the "refinery" location. The losses may enter air, land and water compartments, may be fugitive, accidental or controllable, and will vary by extraction process, material type and physical form. A general, overall methodology is summarized in Figure 10.

The extraction materials balance will usually be geographically specific due to the nature of the deposits. Thus, the first step in the materials balance must be to identify where the material is found. Depending on the scope of the materials balance, one may be limited to a specific region or particular type of deposit. The next step is to identify the general extraction techniques utilized. Is it extracted by strip mining, open pit mining, dredging, etc.? The extraction technique is important in defining and quantifying releases to the environment. In conjunction with this step, one should examine the extraction techniques to identify mechanisms of release and control practices used. This will aid in construction of a generalized block diagram indicating the various sources of release to the environment.

After the basic outline of the materials balance has been completed, one can proceed to obtain data required to quantify the various input and output streams that have been identified. These data will come from a wide variety of sources, including statistics compiled by the Federal government, knowledge of actual extraction operations, and discussion with individuals and organizations involved in this field. The data will include emission factors, loss estimates, accident data, quantities extracted, etc. The completeness and level of detail will be dictated by time constraints, availability of data, use of the materials balance and importance of the extraction process in the overall materials balance. The final step is to quantify the releases based on the data compiled and the general materials balance outline developed in previous steps. It may be

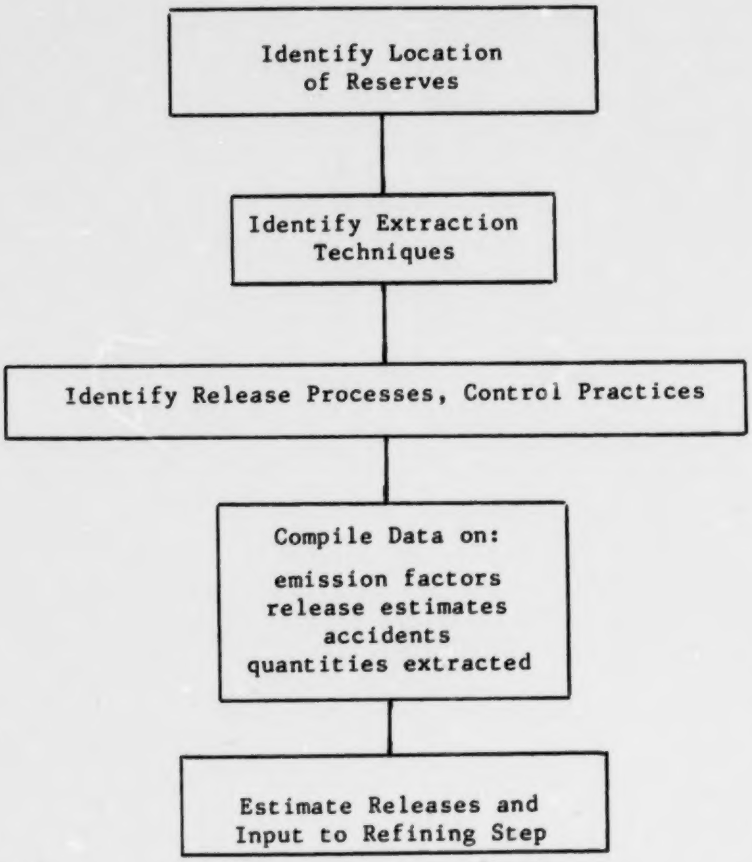
Identify Location of Reserves
Identify Extraction Techniques
Identify Release Processes, Control Practices
Compile Data on:
emission factors
release estimates
accidents
quantities extracted
Estimate Releases and Input to Refining Step

Figure 10. Extraction materials balance flow chart.

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necessary to utilize estimation techniques or the "best judgment" of engineers in order to arrive at release quantities. In addition to quantifying the releases, the balance also serves as input to succeeding steps in the overall materials balance.

Specific Approach

The various steps outlined above can be performed in successively finer levels of detail. The first step in the methodology is the identification of the location of the reserves. Materials are not uniformly dispersed throughout the natural environment, thus it is necessary to have some information on the spatial distribution of the material. Several levels of detail are possible at this point. The most elementary level is simply a map identifying the general location of the material such as a vein of ore or formation of coal. The amount of material in each deposit should also be indicated. The maps can become finer in scale and detail, i.e., from a national map to regional or state maps to county maps. The finest gradation would be the identification of all locations where extraction is being undertaken, the amount extracted annually (or during the period of interest), the amount of reserves remaining and the percent of those available for extraction based on such criteria as economic feasibility, concentration and current technology.

Following, or concurrent with, the identification of reserves, one must ascertain the operations utilized for extraction. The technique will depend on the type of material, its location (i.e., near the surface, in the ocean, deep within the earth), and the quality of the reserve. Typical techniques may include: drilling, dredging, open pit mining, strip mining, shaft mining and deep ocean mining. Several different methods may be employed for a single material depending on the geology involved, location, quality of the deposit, etc. In such cases it would be necessary to associate the technique with the reserves or particular mining/extraction company. A general description of each operation, equipment used and volumes handled should be developed.

50 Lines
to End of
Typing Area

Using the operational descriptions as a basis, one next identifies the methods and/or operations where releases to the environment occur, either in a routine, controllable manner, as, for example, fugitive emissions or as the results of accidents. Disposal and recovery practices must also be examined as points of environmental release. The release mechanism can be directed toward the various environmental compartments of concern, and then subdivided by various methods. For losses to air, one might consider such mechanisms as the wind entraining small particles, emissions due to blasting operations, releases resulting from flares, or losses due to evaporation. Discharges to water could occur from runoff, mine drainage, disposal of tailings, or as a result of dredging operations. Losses to land can result from disposal of treatment sludges, recovery practices, or methods of handling overburden. In general, these disposal releases should be treated in this extraction activity materials balance, rather than later in a disposal materials balance which is directed more toward finished products. In addition to the routine losses, one must also

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identify the potential accidental release processes. These may include such events as oil well explosions, fires, tunnel collapses or spills. A detailed analysis of accidental emissions would involve the development of scenarios, construction of fault trees, and estimation of probabilities of such occurrences. This completes the descriptive, detailed aspects of the materials balance.

The next step is to compile available data and/or develop estimation techniques for performing the quantitative portion of the materials balance. This involves compiling data available in various census publications, from industry organizations and/or companies and, if appropriate, conducting interviews with key individuals. Emission factors either from an operational standpoint or from guidelines (limits) should also be assembled. In cases where information is not available, one will need to make estimates based on "judgments" of various individuals, evaluation of similar operations or materials, or some other defensible means. The level of detail will be influenced by the scope of the materials balance, available resources, time, etc. These data and estimates are then compiled into the final materials balance for extraction and serve as input to the succeeding steps.

Simplified Approach

For various reasons, one may wish to restrict the extraction materials balance in several ways. The balance may be limited to a particular region or by a particular process. It may be that extraction is not a major source of emissions or risk. However, the extraction materials balance may be required for completeness or to provide inputs to succeeding steps. In these instances, it is possible to perform a very limited materials balance, both in terms of time and scope.

This limited analysis consists of identifying the basic compartments to which losses occur. The losses are then quantified by knowing the total amount extracted and the various emission factors that apply to each compartment.

As an example of this limited analysis, consider the following. Mineral A is extracted by strip mining. The loss mechanisms are defined in Figure 11. Assume that available statistics indicate that 10 million metric tons are extracted each year. Assume that review of the literature indicates the emission factors to be:

air: 5×10^{-6} grams/kg extracted
water: 0.05×10^{-3} grams/kg extracted
land: 0.2×10^{-3} grams/kg extracted.

Thus, applying these factors to the total extracted, the output of the materials balance would be:

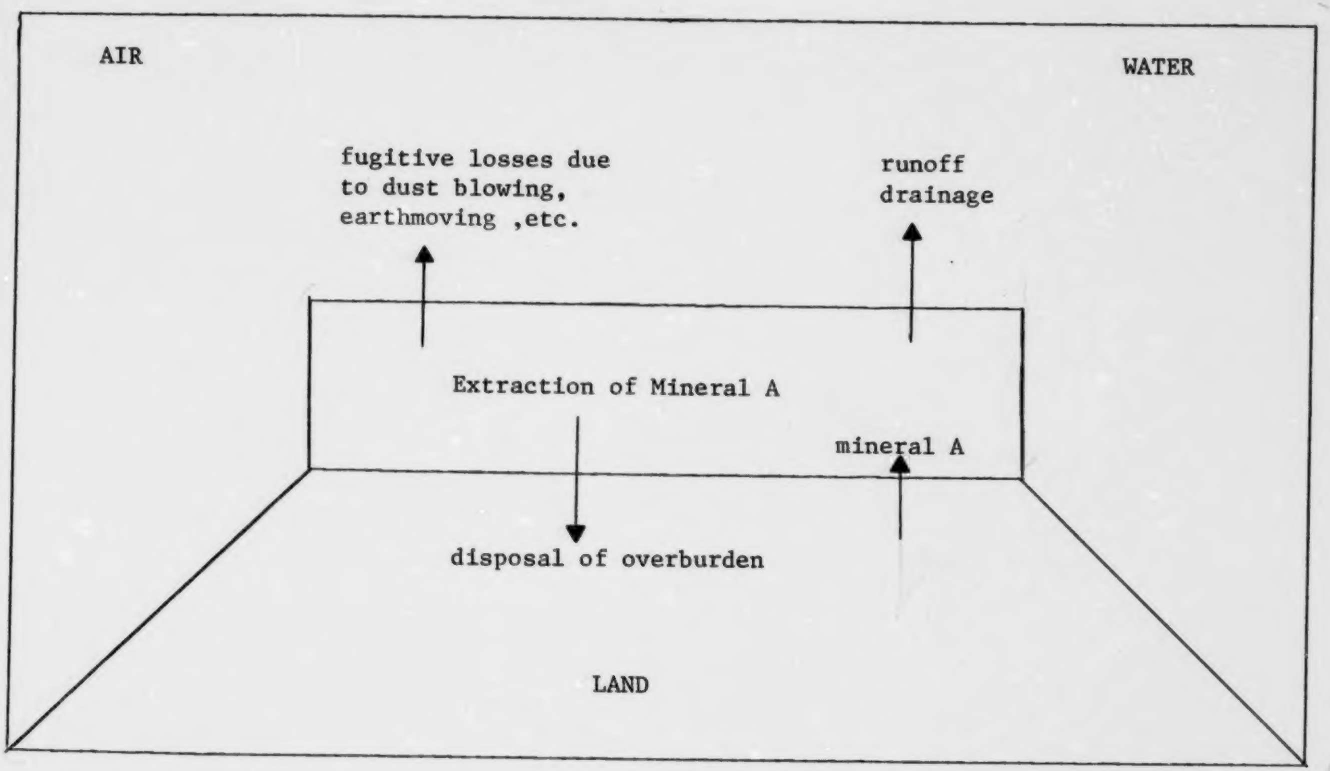
AIR
WATER
fugitive losses due to dust blowing, earthmoving ,etc.
runoff drainage
Extraction of Mineral A
mineral A
disposal of overburden
LAND

Figure 11. Simplified analysis of materials balance for extraction of mineral A.

air: 50 kg/year
water: 500 kg/year
land: 2000 kg/year.

Thus, by simply using data on quantities extracted and estimated emission factors, a limited materials balance analysis of extraction can be performed.

Discussion

In using this extraction materials balance methodology, one will encounter various problems depending on the level of detail desired, time and resources available, and other factors. Information on mineral reserve and quantities extracted is readily available in various publications of the U.S. Bureau of Mines. Description of mining operations can be found in standard references and through discussions with mining engineers. Estimation of releases, however, is much more difficult. Guidelines, if available, provide a basis on which to begin the estimation processes, but further work, data, and discussion will be needed to refine the original estimate and handle those releases where no guidelines have been promulgated.

The uncertainty and the accuracy of the method depends on several factors. Reserves are only estimates whereas production data should be fairly close to actual as they are compiled from data supplied by companies. Releases are difficult to ascertain due primarily to the nature of the emissions and the practices employed in extraction, recovery and disposal. A fault tree analysis of accidents is difficult and will yield very limited additional information.

The methodology can be adapted to the time and resources available. If these are limited, simply gathering available data and using the emission factors and estimates can be done relatively easily and yield an order-of-magnitude estimate. Identifying mine locations, compiling their mining techniques and detailing all the losses can require considerable resources. Thus, one must choose the level of detail based on available resources and the purpose of the materials balance.

Identification of controllable sources should result from the descriptions of the operation. However, the nature of extraction makes it difficult to control losses. Estimating potential exposure routes would require a detailed evaluation of each site, which, although possible, is only realistic on a very limited scale, i.e., a materials balance for a single extraction location. The materials balance should be compatible with current data; however, it may not be in a form to interface with fate data and models.

The simple level of the extraction materials balance methodology is required for any overall materials balance. Going to greater detail is not warranted, in many cases, for several reasons. The opportunities for application of control technology may be limited. Exposure tends to be limited to the immediate area and the individuals who live in the area or work for the company involved in the extraction. Losses from extraction tend to be localized, are in the area where the material occurs naturally and may be minor in terms of total losses. These reasons must be examined on a case by case basis, however.

There are some cases where greater detail may be necessary. If the materials balance is limited to a particular locale, greater detail is possible. Greater detail is desirable when trying to estimate the impact on a particular community or subpopulation. However, care must be exercised in going to finer detail as the results become more sensitive to errors in estimation and accuracy of data compiled on a limited scale.

REFINING ACTIVITIES

General Approach

Refining involves operations which convert the material from the form in which it occurs naturally to a form that is usable in the manufacturing process. The operation is a physical one and usually does not change the chemical structure of the material of interest. Often the refining operation takes place in conjunction with the manufacturing process, as, for example, in an oil refinery or a steel mill. In a refinery, the refining operation (as defined here) is limited to the separation of the crude into various fractions, not processes, such as cracking and polymerization, which result in a chemical change. There is a large amount of overlap in the methodologies for refining and manufacturing but certain distinctions can be made. A general flow diagram for the refining materials balance is presented in Figure 12.

In order to clarify the concept of refining as utilized here, one can consider a materials balance to be performed for phosphorus. Phosphate is present in nature in a matrix composed primarily of clay slimes, silica sand and phosphate pebble. Drag-line operations remove the matrix from the ground and deposit it in an area where it is broken up, then water is added to transport it to the beneficiation plant. The beneficiation plant increases the percentage of bone phosphate lime. Typical equipment may include screens, washers, cyclones and sizers. The concentrated phosphates then undergo various chemical treatments to produce such products as superphosphates, phosphoric acid, and calcium metaphosphate. The beneficiation would constitute the refining portion of an overall materials balance for phosphorus.

The primary objective of the refining materials balance methodology is to identify the flow of the material into various environmental compartments both routinely and non-routinely and the flow into the manufacturing process. Secondary objectives may include identification of releases which are amenable to control and releases which directly affect the population of concern, and compilation of inputs to fate models and risk analyses.

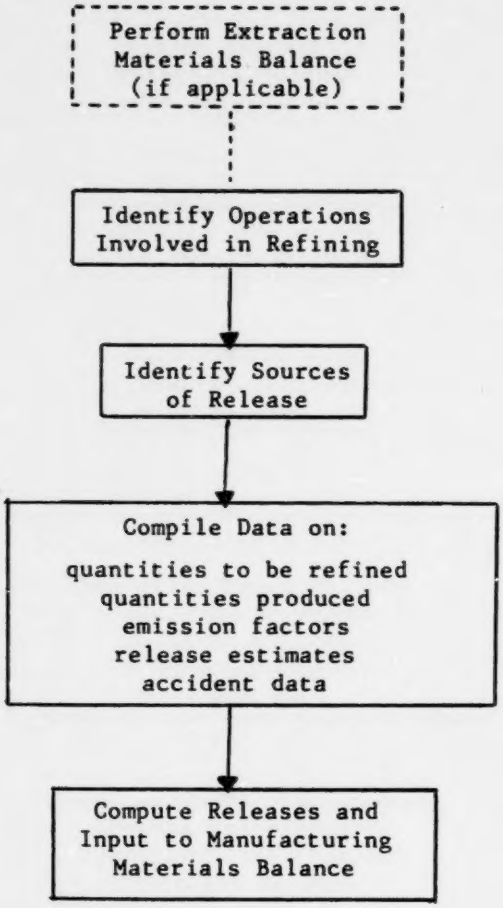
Perform Extraction Materials Balance (if applicable)
Identify Operations Involved in Refining
Identify Sources of Release
Compile Data on:
quantities to be refined
quantities produced
emission factors
release estimates
accident data
Compute Releases and Input to Manufacturing Materials Balance

Figure 12. Refining materials balance flow chart.

The general approach consists of identification of the releases and the quantification of these releases in a suitable manner. The identification step involves the operations and equipment employed in refining. Certain operations and equipment result in specific losses which can be identified. Once these are identified, one must compile data that will aid in their quantification. These data may include quantities refined, emission factors, loss estimates and accident statistics. With these data, one can conduct an analysis of the releases from refining. Some judgment and "best estimates" on the part of knowledgeable experts may be required. These quantities serve as the materials balance for refining and provide inputs to the manufacturing segment.

Specific Approaches

Various levels of detail are involved in each step. The level of detail selected will depend on several basic parameters such as time constraints, purpose, etc. The various steps and levels of the general approach are described in detail in this section.

The first step in the methodology is to identify and assemble information on the various operation involved in refining the material. The operation will be dependent on the state of the raw material and the state of the material required for the manufacturing process as well as other characteristics such as purity, concentration, etc. Typical operations can include: extraction, washing, distillation, smelting, crushing, grinding, evaporation, drying, leaching and mechanical separation. It is likely that the refining operation will involve more than one type of operation or multiple stages of the same operation. One must be careful to separate refining operations from manufacturing processes.

The next level in the identification of operations is the specification of the overall flows in the refining step and the individual inputs and outputs. A general flow diagram of the overall operation should be constructed. In some cases, several options or different steps may be available in the overall operation. All inputs and outputs should be clearly identified, including water requirements, air, solvents used in extraction and any other material that may contact and become "contaminated" with the material of interest. These flow diagrams need only show flows in a qualitative manner at this point. Much of this general information is available in the literature or through limited discussions with industry experts.

The final level of detail in this step would be to actually obtain specific layouts for a typical (or several specific) operations. These drawings would indicate equipment sizes and configurations, location, type and number of pumps, valves, meters, etc., and any control equipment or practices in use. Information on operating conditions, such as temperatures, pressures, solvents and efficiencies may also be included. This type of detailed information can probably only be obtained from the refiner and most likely only at a general level. Additional information will have to come from experience of the individuals involved or knowledge of the operation.

Once the operational flows have been identified, one can proceed to identify points of controllable and fugitive emissions. Controllable quantifiable emissions result from a number of sources such as bottoms from a distillation column, dust from grinding and crushing operations, absorber gases and solvents, and vapors from evaporators as well as pollution control equipment such as electrostatic precipitators and wastewater treatment plants. One must be careful to distinguish between routine and non-routine releases. Routine releases include those that occur as part of the ongoing operations. Non-routine releases occur during shutdown, during periodic maintenance or as a result of an accident. Information on these types of releases comes from discussions with plant operators or through a thorough understanding of the operation. Releases due to accidents--explosions, fire, spills--must be dealt with through scenario development and fault tree analysis.

In conjunction with these steps, one can be assembling data to be used in the final materials balance computation. The types of data gathered and the level of detail will depend on the purpose, availability of data and resources committed to the analysis. Gross information on inputs can be obtained from the extraction materials balance or from various census data and industry publications. Finer detail and accuracy would require a survey of companies involved in refining. This type of information is usually not available and so is probably beyond the scope or feasibility of a materials balance.

Information on output of the material from the refining operation will not be readily available. The primary reason for this is that refining and manufacturing are usually done in a continuous operation. It is unusual to have a company perform only refining as it is defined here. For example, the output from an oil refinery is not simply the various fractions resulting from separation of the crude oil but rather a wide mix of hydrocarbon products such as fuels, gasoline, alcohols, ethers and various other solvents. Thus, the outputs will rely on the information developed when describing the overall process. For this reason, it is important to have data on typical flows, efficiencies, by-products, etc.

Information needed to estimate releases should also be compiled. One source is any guidelines on emissions promulgated by Federal, state or local regulatory agencies. These guidelines present a means of obtaining upper bound estimates of losses. Information from engineering evaluations, refiners' experience, equipment manufacturers and others may help to establish typical emission rates or provide data that are useful in the final calculation. Information on accidental releases, where available, should also be compiled.

With the necessary background information assembled, one can proceed to perform the quantitative materials balance. Again, several levels of detail are possible and correspond to purpose of the work and the background information developed. The most basic approach is simply to use emission factors with the corresponding data on quantities refined and obtain a gross estimate. Thus, the equation is of the form:

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tons of material refine per year x pounds
of emissions per ton refined = pounds of
emissions per year.

A separate factor is used for each environmental compartment.

The next level of detail is an engineering analysis of a typical operation. This involves using information on the operation itself, efficiencies and any emission factors which may be available. An example would be using recovery efficiency to estimate output and then partitioning the losses to various streams based on operating mode, discharge points, etc. Efficiencies can also be used in conjunction with pollution control equipment. This technique may be applied to each operation in the overall refining operation as well as each general type of operation. This type of analysis gives more specific information and a better understanding of potential control methods. These estimates of losses are then applied on a general overall basis to the total amount of material refined to obtain the various outputs.

The finest level of detail in estimating losses is to perform a plant specific materials balance. For this, one must identify all companies and their plants involved in refining. A detailed analysis is then made, based on general flows, operations utilized, quantities refined, etc. Emission factors for pumps, valves, etc., can also be applied to specific plant layouts. This type of analysis will be very difficult to perform without cooperation from industry and cannot be attempted in cases where a large number of plants exist or many companies are involved. This approach is more suited to a local or, at most, regional scale materials balance.

Accidental losses will probably require the development of scenarios and the use of fault tree analyses. Some assistance and guidance can be obtained through review of previous accidents and through discussions with plant operators. Probabilities for valve failures, spills, etc., are available in the literature.

Simplified Approach

A simplified refining materials balance might be performed for several reasons. The release from this operation may be small. This portion of the materials balance may be a subset of an entire plant balance, including manufacturing and processing in addition to refining. The refining step may be limited to a single operation, which makes a limited analysis relatively straightforward. The limited analysis involves identification of release mechanisms and then quantification of losses in a simplified manner, usually via emission factors and throughput data.

As a hypothetical example of the simplified analysis, consider the benefication of an ore. One can identify typical release mechanisms as outlined in Figure 13. Various pieces of equipment can be associated with

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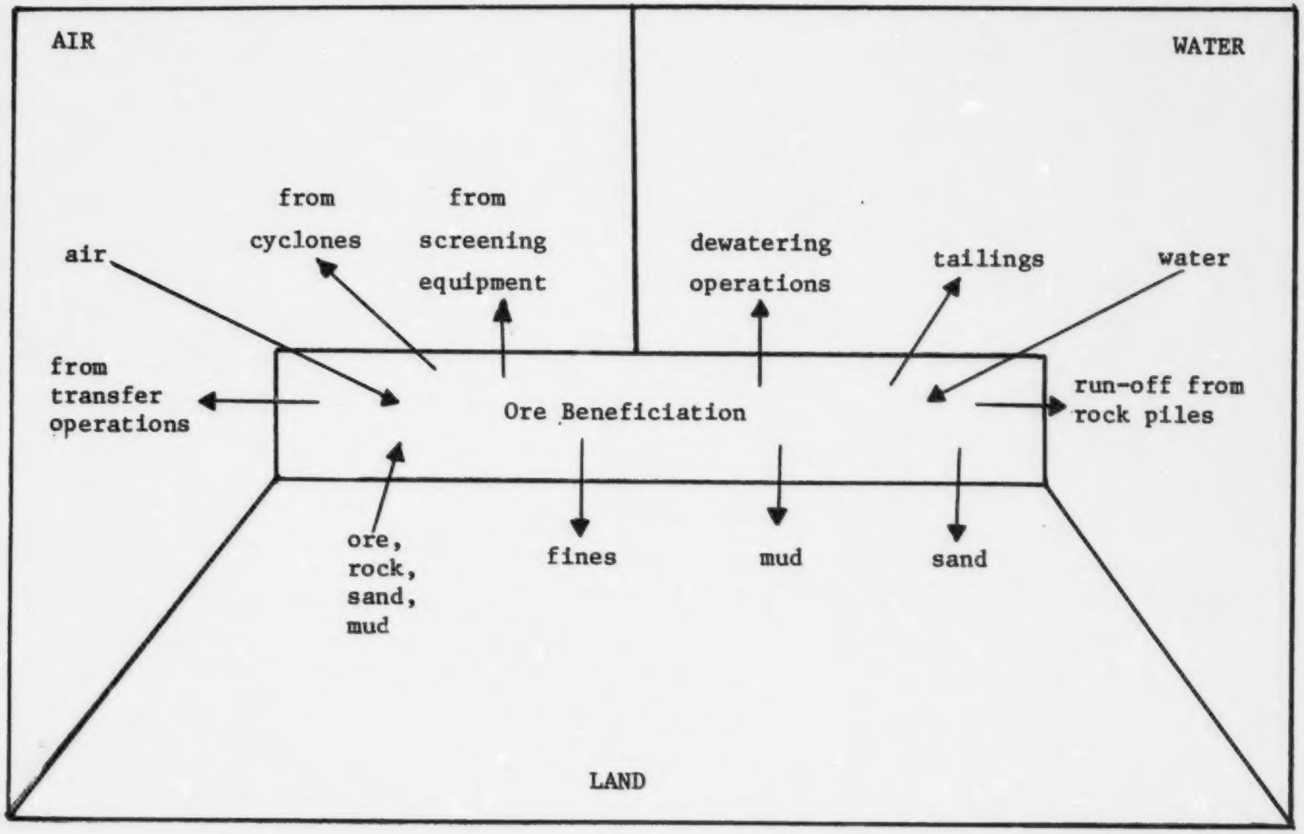

AIR
WATER
air
from cyclones
from screening equipment
dewatering operations
tailings
water
from transfer operations
Ore Beneficiation
run-off from rock piles
ore, rock, sand, mud
fines
mud
sand
LAND

Figure 13. Simplified materials balance analysis of ore beneficiation.

the various operations. Emission factors can be compiled in a matrix for each general equipment category and environmental compartments. An example of a possible matrix is presented in Table 2. By multiplying the emissions factors by the quantities processed, one obtains the materials balance.

TABLE 2. HYPOTHETICAL EMISSION FACTORS* BY RELEASE POINTS AND ENVIRONMENTAL COMPARTMENTS

	Environmental Compartments		
Points of Loss	Air	Land	Water
Cyclones	1×10^{-6}	4×10^{-6}	-
Screens	$.5 \times 10^{-6}$	-	-
Belts	$.5 \times 10^{-6}$	-	-
Washers	-	$.5 \times 10^{-6}$	1.5×10^{-6}
Flotation Tanks	-	$.1 \times 10^{-6}$	5×10^{-6}
Inclined Screw	$.5 \times 10^{-6}$	-	-
Dewatering Operations	-	1×10^{-6}	$.5 \times 10^{-6}$
Runoff	-	$.05 \times 10^{-6}$	1.2×10^{-6}

*Values are expressed in grams of ore emitted per kg processed and are not intended to represent true values.

Based on 25 million metric tons processed per year, the following results are obtained:

Air: 62.5 kg/year
Land: 141.25 kg/year
Water: 205 kg/year

An even coarser analysis is possible by simply using an overall emission factor for each environmental compartment. This limited analysis serves to give a general estimate of the magnitude of losses during refining operations.

Discussion

As indicated in the discussion of each step, one can go to varying degrees of detail in conducting the materials balance. The level used will depend upon the time for performance of the work, the human resources that are devoted to the effort, the type and accuracy of information that is available, the scale of the materials balance and the material itself. The finer the detail, the more time and resources required and the greater the level of certainty and accuracy.

More complete use of this methodology may allow identification of controllable sources. This is possible only through a review of the specific operations involved in refining. Greater level of detail permits for comprehensiveness in coverage and depth of resolution, and permits one to better define and understand possible exposure routes. In these cases, any monitoring data can be utilized to verify the balance or provide a means of deriving overall emission factors.

The simplified level of this methodology is primarily for use in cases where only gross estimates are desired. To obtain better resolution one must, at least, have some basic understanding of the physical operation involved. Thus, even if time and resources are limited, it is worthwhile to gather data on and perform an analysis of the operations involved. The additional effort required for the subsequent levels of detail gives resolution to the materials balance that makes it more useful and provides information for use in various areas of regulation, control, etc.

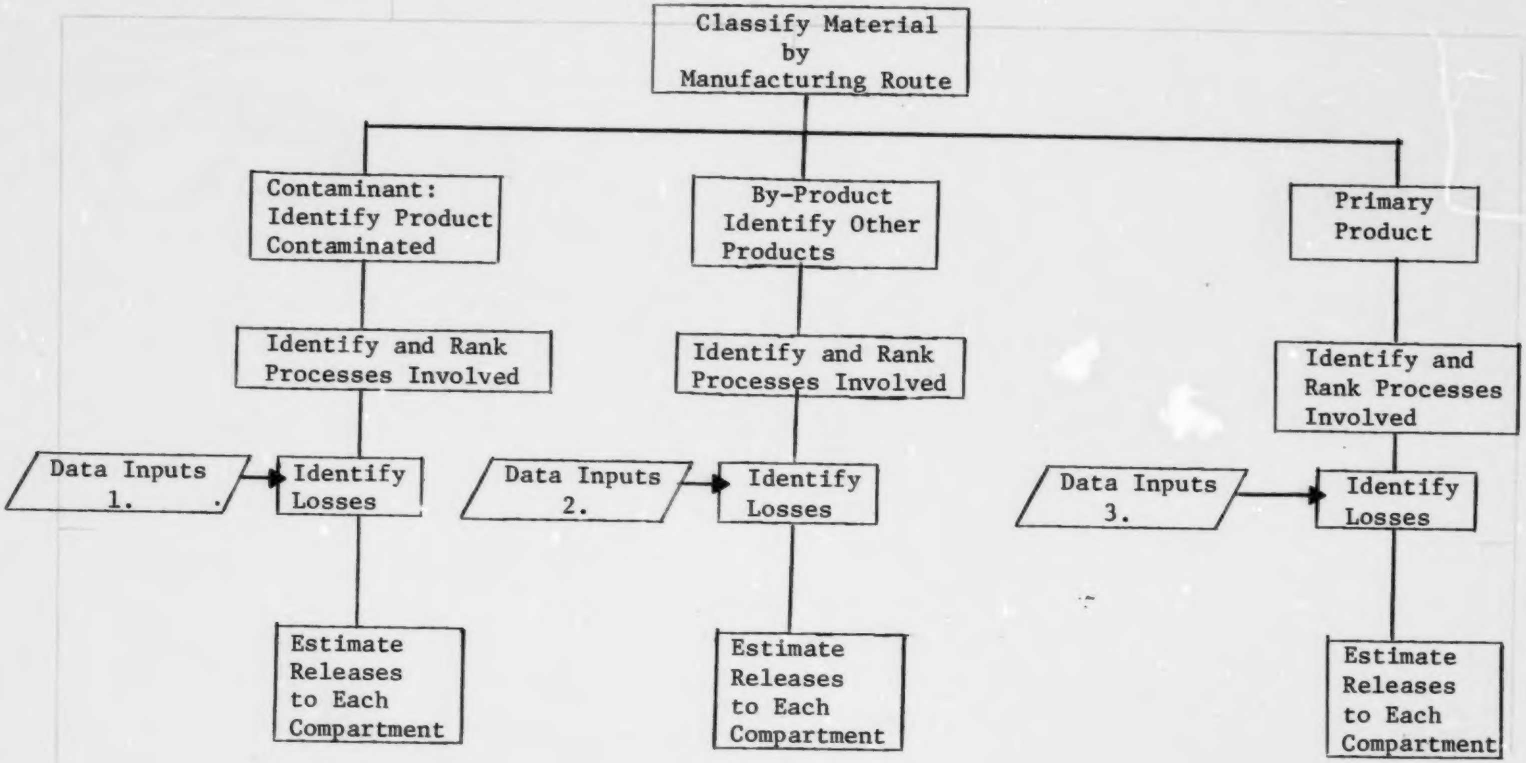
MANUFACTURING ACTIVITIES

General Approach

For synthetic materials, the manufacturing segment would represent the initial step in developing the materials balance. The manufacture of the synthetic material is a likely and significant contributor to environmental loadings due to industrial activity, and hence, is of primary interest in the materials balance. The manufacturing segment is defined to consist of those processes that convert the raw or refined material to a form required for further processing or fabrication of a final product. These processes involve chemical transformation of one or more materials into another, chemically different, material. Manufacturing may occur in conjunction with the refining or processing operations. It may be difficult to separate these industrial activities in terms of their contributions to environmental releases. Figure 14 presents a diagram of the general methodology for the manufacturing segment of the materials balance.

The objectives of the manufacturing segment of materials balance are the estimation of the expected range and quantity of direct releases to the environmental compartments due to manufacturing. In line with these objectives, an examination should be conducted of the form of a chemical or material release, geographic distribution of release, the environmental compartment receiving the release, and the release concentration as a function of time during which release occurs.

The initial step in the general approach to the manufacturing segment of the materials balance is the classification of the chemical or material. A material generated by a manufacturing process is most likely to fall in one of three categories: materials that are produced as the primary product, materials that are by-products (either with or without economic value), and materials that are contaminants of other materials. Any given


Classify Material by Manufacturing Route
Contaminant: Identify Product Contaminated
By-Product Identify Other Products
Primary Product
Identify and Rank Processes Involved
Identify and Rank Processes Involved
Identify and Rank Processes Involved
Data Inputs 1.
Identify Losses
Data Inputs 2.
Identify Losses
Data Inputs 3.
Identify Losses
Estimate Releases to Each Compartment
Estimate Releases to Each Compartment
Estimate Releases to Each Compartment

1. Chemistry, process variables, balance for contaminated products, etc.
2. Process variables, emission factors, etc.
3. Process variables, emission factors, production volumes, etc.

Figure 14. General flow diagram for manufacturing.

material may fall within two or more of these classifications. The classification of the materials is followed by identification of the principal and alternative manufacturing routes. Because releases to the environment may occur at any step in the manufacturing process, it is appropriate to examine in detail the steps involved in the manufacture of the material. It is also important to examine and rank, in terms of relative importance, the alternative routes which may yield the material.

Identification of the manufacturing route and associated operations could include the preparation of a basic flow diagram of the steps involved. Composition of the input, output and intermediate streams should be noted, along with identification of process equipment, including any pollution control equipment that may be used. In addition, the various reactions, both primary and secondary, that are involved in the process should be specified. The basic operating conditions, including temperature, pressure, reaction constants, and other process variables, should also be noted. The summation of the basic chemical reactions, together with the notation of the critical operating parameters might also be included.

Construction of the process flow diagram enables identification of points where releases may occur. At minimum, identification of the form of releases, i.e., as solids, liquids or gases, is possible through examination of the process flow diagram. A more detailed study of the manufacturing route may enable a more accurate characterization of the process waste streams and the mechanisms whereby releases occur. In particular, an understanding of the chemical reactions involved will assist in identifying constituents of the environmental releases.

In summary, the basic data requirements of the manufacturing segment of the materials balance include:

- Identification of the manufacturing routes and chemical reactions involved,
- The quantity of product manufactured,
- Process variables,
- Operating efficiencies,
- Emission factors,
- Concentration of contaminants, etc.

This information may be obtained through a review of the literature, or through field work such as a survey of manufacturers, trade associations, government agencies, etc.

Specific Approaches

Method of Analysis--

Routine releases occur during the on-going process, and include all waste streams. These include losses that are planned for such as those occurring during cleaning, periodic maintenance, and shutdown, as well as those that are subject to controls. Data requirements for the estimation of the manufacturing related losses include: volume of production, process variables, operating efficiencies, emission factors, etc.

Specific approaches to characterize and quantify the extent of materials release may be based on precise calculation or, more likely, estimation techniques. The data collection effort should be structured to yield detailed information on the physical, chemical, and engineering properties, as well as data on the production rate and volume. From this information, an objective would be to calculate a conversion rate, on which to base an estimate of likely material release. This estimate could be verified through the literature review and field work.

An alternate route would be to examine data on the range of concentration of the material in plant effluent. Depending on the material, this information may be available in data bases such as STORET maintained by EPA. If it can be established that the sample analyses are typical, and if the flow rates can be determined, it may then be possible to assess from this information environmental loadings due to manufacture. In any event, information developed from analysis of the manufacturing process can be used as a check that release estimates are consistent with observations of plant effluent concentrations.

The literature review may also yield information on observed concentrations of the material in the environment, which again may be used to verify that estimation of releases are consistent with environmental concentrations.

Non-routine Releases--

Non-routine releases include excursions of material which occur in an unusual and/or uncontrolled manner. These include accidental releases, which may occur in the form of spills or leaks; fugitive releases, such as the escape of wind blown particles; and catastrophic releases, such as may occur under conditions of fire, explosion, etc. In general, non-routine releases are determined by estimation, based on judgment or statistically valid assumptions of the likelihood and magnitude of occurrence.

An Example: Phthalate Esters--

As an example of a materials balance for manufacturing, one can consider phthalate esters. Information in the literature indicates that yields in excess of 95 percent are obtained for the conversion of phthalic anhydride to phthalate esters. It is assumed that any material not accounted for in final products is found in the waste streams. Two sources of loss are decanting operations and purification operations. Literature sources estimate production loss to range between 0.2 percent and 0.5 percent. It is also assumed that the majority of the releases are to water, given the nature of the process and the material. In 1977, the U.S. produced 1202.4×10^6 pounds of phthalate esters of which 1108.8×10^6 pounds was used for manufacturing products in the United States. The release to waters in 1977 from manufacturing was

$$.005 \times 1108.8 \times 10^6 \text{ lb} = 5.544 \times 10^6 \text{ pounds}$$

Simplified Methods of Analysis

A simplified method of analysis would involve documentation of a release rate for the material from the literature followed by straightforward calculation of the release estimates. This approach would obviate the necessity of calculating conversion rates, based on the chemical reactions, raw material inputs, and other data. In practice, however, this "key" to the estimation of release is not always readily available. An alternative approach might involve estimation based on an assumption concerning the proportion of the total production released during manufacturing, where the factor used to derive the estimate is based on judgment rather than documentation. Industry experience forms a firm basis for such judgment.

Discussion

The estimation of environmental releases from manufacturing may be subject to a large error, depending on the type and accuracy of data inputs to the analysis. It may, therefore, be appropriate to specify a range for the estimated release. Manufacturing releases may be assumed to occur prior to tabulation of production data, and hence, are not accounted for in reports of production. The performance of a materials balance based on reported production figures must, therefore, take into account releases which may occur during the stages of manufacture. It may be noted that in the example cited above, the estimate of release was based on published sources which quantified a range of potential release from a particular stage of manufacturing. For the phthalate esters, it is believed that the decantation and purification stages are the primary sources of release from manufacturing. For other products, other stages could be of significantly greater importance.

PROCESSING ACTIVITIES

General Approach

The processing segment of the materials balance represents a stage in the materials flow intermediate between the extraction or manufacture and use of a product. The performance of this portion of the materials balance, together with those for extraction, refining, and manufacturing, yields estimates of contributions to environmental loadings for the

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chemical of interest from industrial activity. The processing segment is defined to include and consider the physical processes by which materials are incorporated or transformed, into products for consumption. These processes may result in releases to the environment by virtue of the process employed and/or nature and characteristics of the materials used.

Figure 15 presents a general flow diagram for this segment. The goals of the "processing segment" of the materials balance are the estimation of lower and upper bounds of direct releases to environmental compartments due to processing, examination of the form of the chemical or material released, geographic distribution of the release, effects over time, and initial analysis of how such processing may influence environmental loadings over time. In this respect, the processing segment provides important inputs to the analysis of the use and disposal segments of materials balance on products composed of or containing the material of interest. Environmental loadings due to processing are generally distinguished from extraction, refining, and manufacturing loadings by the fact that they are more closely associated with preparation of a finished product. Hence, these releases may contain other materials or environmental contaminants added in processing. This is in contrast to extraction or refining losses, which may contain contaminants removed from the subject material prior to processing. Releases from the process stream may occur either as routine events (e.g., discharge of wastes); or as non-routine (i.e., accidental spills, leaks, or other unplanned losses.) The materials balance methodology for the processing segment must, therefore, take into account both types of losses, and yield estimates of releases to the environment as a result of such losses.

The framework of the analysis depends on background information pertaining to the primary and alternative processes which utilize or involve the subject chemical. The identification of the processes, together with compilation of process descriptions, are the initial steps taken in developing the analysis. The processes to be identified include those where the end result is the incorporation or transformation of the material into intermediate and/or finished products, as well as those which may result in the formation of the subject material as a by- or co-product. Other related processes might also be considered. For example, the subject material may be known to be present as a contaminant in product or waste streams generated from processing of other products. The processing of such associated products would thus be considered part of the processing segment of the materials balance for the chemical of interest. In addition, naturally occurring, as opposed to anthropogenic, processes may also be a factor in the materials balance, and should be identified in this stage of the analysis.

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The process description and process flow diagram are useful tools for identifying raw material requirements, chemical reactions and physical changes, stages of the process which may result in releases to the environment, and waste materials which may be generated. This information is used for the identification of types and sources of process releases, and for preliminary allocation of releases to the environmental compartment.

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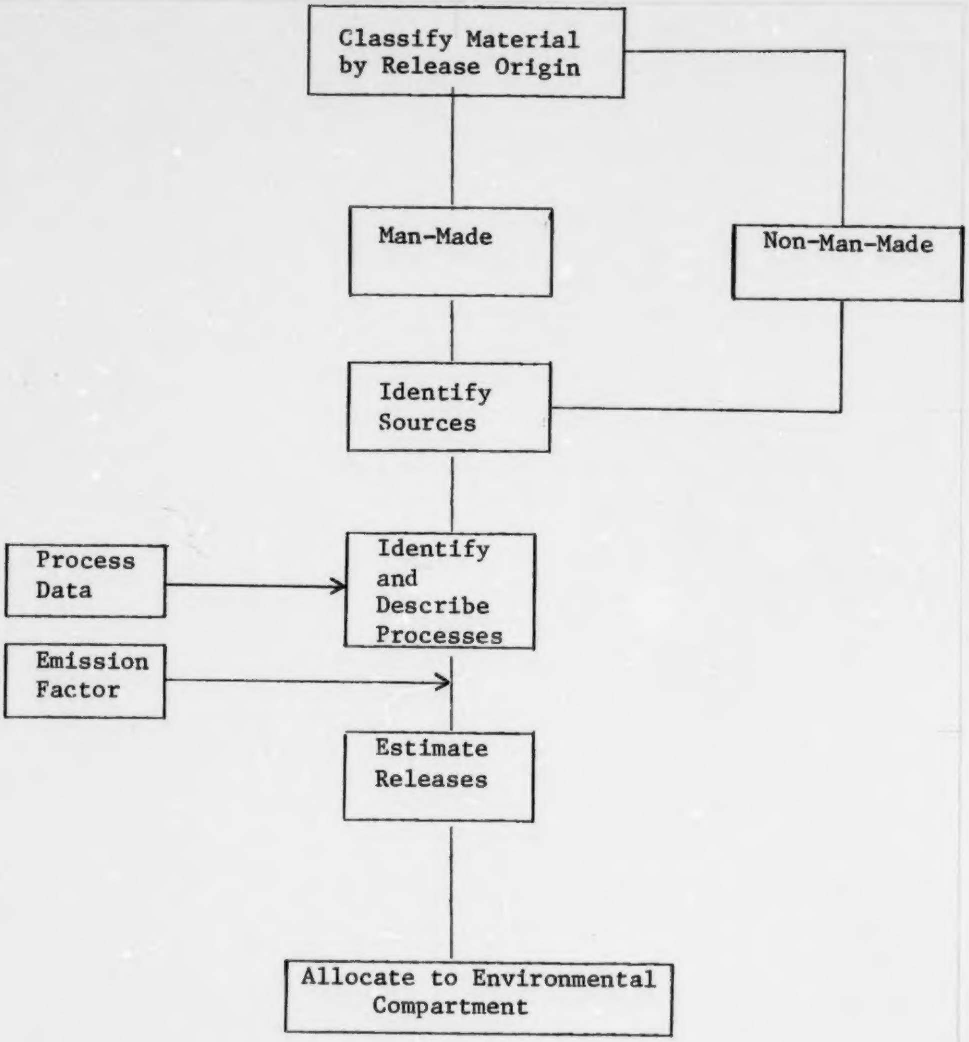
Classify Material by Release Origin
Man-Made
Non-Man-Made
Identify Sources
Process Data
Identify and Describe Processes
Emission Factor
Estimate Releases
Allocate to Environmental Compartment

Figure 15. General flow diagram for processing segment.

From information pertaining to the quantity of raw material inputs, operating efficiencies, and product output, data regarding the characterization and composition of the process waste streams may be obtained or estimated. To the extent that this information is quantified, the process description provides a basis on which the calculation of release estimates can be made. Comparisons of the descriptions of alternative processes can be made to examine how releases from these processes may differ in character, quantity, and contribution to environmental loadings of the substance.

A review of the literature is a component of the general methodology for the processing segment because of the needs for current and historical consumption of the processed material, and production and trade data on the processed material; for current and background information on the primary and alternate processes employed; for identification of control practices and efficiencies; and for other data needs (e.g., raw material inputs, sample data, emission or loss factors, etc.). The material compiled via this route can supplement data gathered by other methods, such as interviews with processors, trade associations, government agencies, and others involved in the field.

Specific Approaches

Routine Releases--

Routine releases are defined as occurring from material losses subject to process controls or otherwise planned for in the general operation and maintenance of process equipment. These emissions include waste material released after treatment by air or water pollution control equipment. Such treatment, operating at optimal levels of effectiveness, would be expected to have efficiencies of less than 100%, resulting in some releases of material to the environment. These releases should be accounted for in the materials balance. Evaluation of these releases are described below in terms of an emission factor, determined quantitatively by analysis of control processes and efficiencies, or through reference to the literature or industry sources. Other planned losses might include material residues, tailings, cuttings, etc., which would accumulate in process handling equipment or other areas in the work space, and be collected for disposal by routine plant cleaning, maintenance, and other procedures.

Based on information obtained from the literature or knowledge of the process, a first step is to specify the environmental compartment most likely to receive releases of the material of interest. An example of an approach, where the emission factors have been identified, is presented below as the general equation:

$$x_1 = y_1 \left[(a_1) + (a_2) + (a_3)\right] \qquad (1)$$

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where

x_1 = total release (kg/year)

y_1 = volume processed (kg/year)

a_{1-3} = emission factors.

This example assumes that processing releases are distributed among the various environmental compartments. In a modified form, the equation could specify only waterborne or other releases as required, by use of the appropriate coefficients. The example also assumes that all losses are subject to disposal, and a portion of losses in a particular form are actually released to the environment. The emission factor specifies the proportion of production (y_1) likely to be released in a particular form (i.e., vapor phase, solid phase, etc.). The equation expresses the release of material as a function of mass or volume and time.

In the example, it is assumed that a fraction of the total volume processed is rendered unusable, is not recycled, and is lost in the form of emissions to the atmosphere. The volume of these emissions are determined first by estimating the fraction of material likely to be available for release by this route. This fraction is expressed by the term a_1y_1, with the coefficient a_1 referring to that portion of the available volume expected to be vented to the atmosphere. Estimation of a_1, the emission factor, is based on "typical" efficiencies of equipment (e.g., electrostatic precipitators or venturi scrubbers) most likely used to control air emissions. It is also assumed that the portion of available volume of material not vented is converted to another form, disposed of by other means (e.g., landfilled as sludge) and hence, is by definition accounted for elsewhere. It is further assumed that an additional fraction of the material processed is released to land. This fraction is represented in the equation by the term a_2y_1, where a_2 is the factor--determined judgmentally or by documentation of the process--which expresses the percentage of the total volume (y_1) available for release as solids. Similarly, a_3y_1 is used to describe waterborne releases.

10 Lines to End of Typing Area

The factors used to obtain estimates of releases in this example may be considered process-specific; that is, they are based on operating variables "typically" encountered in a specific process. Calculation of the coefficients also requires detailed information regarding the physical and chemical properties of the material. Hence, the emission factors are also material-specific. The estimates of losses derived by use of such factors are considered "gross," in that they may be used to quickly arrive at estimates of material released on an industry-wide basis.

More detailed information on waste streams may be obtained from sampling data collected in the course of scientific investigations, permit applications, required plant effluent and environmental monitoring, or other sources in the public domain. To the extent that these sources are available, they permit detailed characterization of waste streams in terms

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of their constituents and concentrations. Such information can be used to check that the estimates generated are in an appropriate range. While such data may not be compiled on a process-specific basis, information regarding the total volume of processed material, the geographic distribution of processing facilities, the "typical" concentration of the substance of interest in the waste streams and ambient environment, and the relative importance of alternative processes enable estimation and allocation of releases on process- and compartmental-special bases.

Releases to Water--

Evaluation of waterborne releases requires initial background on the properties of the material and the process. For example, it is pertinent to know in what form the material enters the process, whether it is miscible in water or solvents, and whether the substance of interest is likely to come into contact with solvating materials. When the presence of the material in waterborne discharge is established, information on the expected concentration of the material in the effluent stream can be important to estimation of releases to water, since such information can facilitate calculation of a water-release coefficient. In the absence of such information, it may be possible to document a coefficient from the literature, or to arrive at an estimate by inference, given sufficient data for calculation of release estimates for other compartments.

An information source which can prove useful is the STORET data base maintained by the EPA. This data base can be used to analyze water quality sampling data for a diverse group of chemicals and to compare ambient and effluent concentrations, geographic distribution of concentration, etc. In conjunction with the information obtained from the literature review and other sources, including industry, other government sources, etc., it may be possible to use this information to allocate a fraction of the observed environmental concentrations to processing operations. If these operations are not indicated by other evidence to be a major contributor in a particular location, or if there is a likelihood that observed concentrations may be due to non-processing or unrelated sources, such allocation is made more difficult. In any event, the data base can be used as a general check on the validity of the estimates.

10 Lines to End of Typing Area

Releases to Air--

As with releases to water, estimation of air emissions are likely to be process-specific; hence, estimation techniques utilize operating parameters and emission factors appropriate to the process. To evaluate the potential problem of air emissions, the physical and chemical properties of the substance of interest must be examined together with parameters (e.g., operating temperatures) which may affect the release of the material in the gaseous or vapor phase.

Weighting of the volume of material processed by the emission factor, which may be derived from an analysis of operating efficiencies, material characterization and process parameters, and by the expected proportion

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of material available for discharge to the compartment yields an estimate of the release to the compartment. This method can be used to evaluate the term of the general equation above for atmospheric emissions, as well as for releases to other compartments.

Similarly to the approach described for releases to water, data bases, such as SAROD, can be used to analyze air quality trends for certain pollutant parameters. Other data bases, such as NEDS, may also be used to test the validity of processing release estimates. State and local agencies may also compile air quality data, which can be used as guidelines for checking estimates.

Releases to Land--

Solid waste may constitute a significant fraction of releases to the environment due to processing. The approach described above, utilizing coefficients of loss and emissions, may also be appropriate for the estimation of releases to the land. Recent legislation, such as the Resource Conservation and Recovery Act and Toxic Substance Control Act, may increase the need for, and availability of, data bases on land-based disposal. Access to such information could assist in performing the materials balance.

Non-Routine Releases--

Non-routine releases may occur in the form of fugitive or accidental losses. Such losses include those resulting from spills, leaks, ruptures, explosions and other uncontrolled releases to the environment. Estimation of such releases is likely to be subject to a greater margin of error than estimation of routine releases, due to the unpredictable nature of the events resulting in the excursion of material by these routes. Statistical analysis of the occurrence of an event (e.g., explosions at plants producing the material) may define a probability distribution, which can be used to develop a model relating the likelihood of such an occurrence to the extent of releases which would be expected to result. Design or engineering data for the process under examination may form the basis for estimates of releases by leakage from pumps, joints, pipes, and other transference and handling equipment. In the absence of any such data for the estimation of non-routine releases, judgmental or "best guess" estimates may have to be substituted.

An Example: The Phthalate Esters--

Identification of processes--The phthalate esters are subjected to several stages of processing, depending on the intended end use. Most phthalate ester production is used to provide plasticizers, principally for flexible polyvinyl chloride applications. In this end use, the plasticizer is compounded with PVC resin and other additives to form the plastic. Other processing to form flexible plastic products includes calendering, extrusion, injection molding, rotational casting, etc. Butyl benzyl phthalate (BBP) is a phthalate ester used in this application.

Identify emission sources--Compounding of the resin and plasticizer takes place at elevated temperatures, resulting in some volatilization of the plasticizer. Subsequent processing of plasticized PVC is also likely to take place at temperature which may result in volatilization of the plasticizers. Fabrication of PVC products also results in generation of wastes which may release phthalate esters to the environment.

Non-plasticizer uses of the phthalate esters include use in pesticides and insect repellants, as dispersants, carriers, etc. These uses account for only about 2 to 3% of the domestic supply, however.

Observations of ambient concentrations of phthalate esters in the environment have been made, indicating natural sources. However, man-made sources are believed to be the principal sources of release to the environment.

Estimate Releases

Processing of plasticized PVC is estimated to result in volatilization of 2 to 4% of the phthalate esters used in this application. This includes volatilization which occurs during compounding, calendering, extrusion, injection molding, etc., and other processes which occur at elevated temperatures.

Processing of plasticized PVC results in generation of other, principally solid wastes. These wastes range from 1 to 12% of the material processed, depending on the process and product.

For BBP, this range is between 4 and 7%. Table 3 summarizes the calculations for the processing release estimates.

Simplified Methods of Analysis

A simplified approach to determining the amount of material available from processing for release to the environment is based on reported conversion efficiencies in the processing step. The major assumption in this approach is that all materials not converted, or utilized in the final product, are released to the environment as waste. The subsequent step of this level of analysis is to allocate a fraction of the release to each environmental compartment. This allocation is preferably based on documentation from the literature, but may be derived judgmentally or on a "best guess" basis.

In summary, this approach may consist of the following steps:

- Determination of the quantity of material produced and/or processed.
- Estimation of total release related to processing, based on conversion efficiencies.
- Allocation of processing releases to environmental compartments.

Table 3. SAMPLE PROCESSING-RELATED MATERIALS BALANCE CALCULATION FOR BUTYL BENZYL PHTHALATE

Estimated U.S. Supply - 122 mm lbs.
Available Supply - 121.88 mm lbs.

Product	Volatilization Losses: Total Amount (mm lb.)	Volatilization Losses: Factor	Volatilization Losses: Amount Volatilized (mm lb.)	Losses From Other Processing: Waste Factor	Losses From Other Processing: Waste Amount (mm lb.)	Estimate of Total Release (mm lb.)
Other polymers	18.28	.03	.55	0.05	.89	1.44
Plasticized PVC						
Vinyl flooring	93.24	.03	2.80	0.01	.90	3.70
Other uses	10.36	.03	.31	0.07	.73	1.04
Total	121.88		3.66		2.52	6.18

Released to Environmental Compartments

Volatilization Losses: Air: Factor[1]	Volatilization Losses: Air: Amount	Volatilization Losses: Water: Factor[1]	Volatilization Losses: Water: Amount	Other Processing Waste: Land: Factor	Other Processing Waste: Land: Amount
.35	.19	.65	.36	1.0	.89
	.97		1.83		.90
	.11	———	.20	———	.73
	1.27		2.38		2.52

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[1] It is estimated that of the volatization losses .35 is released to air and .65 to water because of control systems in use.

Discussion: Complications and Problems

A potential problem in the performance of the materials balance may arise in distinguishing between the contributions of the various types of industrial activity that may result in environmental releases of the material. Attribution of a fraction of the environmental concentration to processing may not be straightforward if the industrial activities (i.e., refining, manufacturing, processing) are all carried out at the same site and/or if distinctions between the activities are not clear. Another potential constraint is the lack of available literature, and the refusal of industry sources to discuss a proprietary process. Such constraints may hamper the development of a process description, derivation of emission factors, and initial allocation of environmental releases. Where data deficiency forces the use of judgmental estimates, the assumptions underlying the estimates should be delineated, and a margin for error specified. The contributions of the processing segment should be reconciled with other segments of the materials balance and with observed concentrations in the environment.

TRANSPORTATION ACTIVITIES

General Approach

The objective of the transportation portion of the materials balance is an estimate of upper and lower limit releases of chemicals of interest as functions of time and location. Unlike the case of manufacturing, the transportation-related releases have no documented process flow diagrams on which to base release estimates. The objectives of the transportation function are all aimed at complete containment; therefore, fugitive and accidental losses are the two main categories of interest.

The materials balance release estimates from transportation systems make use of several standard techniques from other fields. First, the network distribution of transportation by mode, geography, and time must be specified for the product or chemical from either statistics or a network flow simulation. Second, the fugitive losses are estimated from emission factors used in air pollution or water pollution studies. Finally, the very complex area of accidental releases is examined by standard techniques of risk analysis to establish reasonable bounds for accidental releases to environmental compartments. The overall approach to this type of materials balance is shown in Figure 16.

Specific Approaches

Modal Allocation--

The analysis begins with a compilation or computation of modal allocations of materials flows. This provides some idea as to what fraction of the material is transported by truck, rail, vessel, or pipeline. In order to satisfy the objectives of the materials balance, this step can assume the proportions of a network calculation that distributes

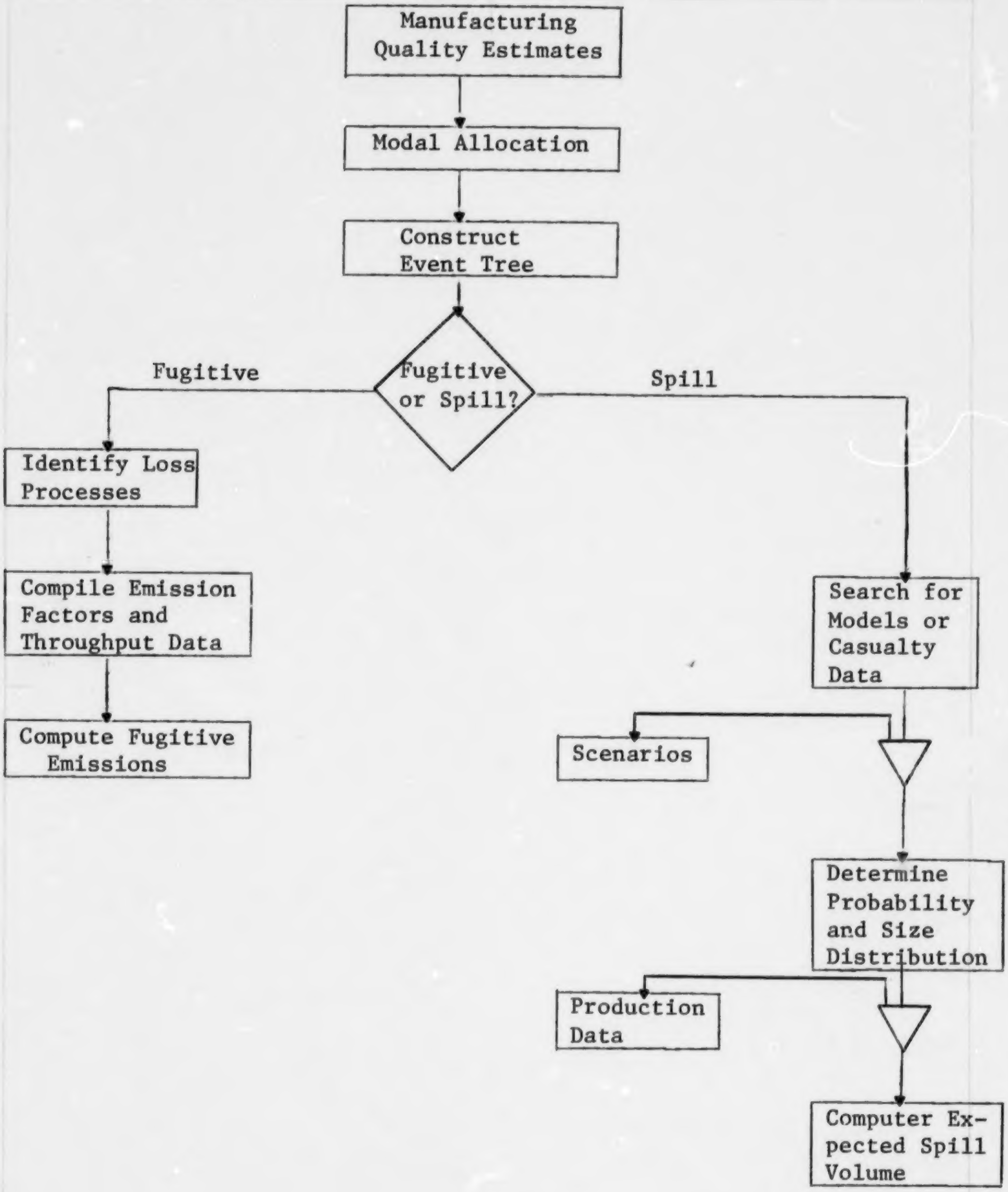
Manufacturing Quality Estimates
Modal Allocation
Construct Event Tree
Fugitive or Spill?
Fugitive
Spill
Identify Loss Processes
Compile Emission Factors and Throughput Data
Compute Fugitive Emissions
Search for Models or Casualty Data
Scenarios
Determine Probability and Size Distribution
Production Data
Computer Expected Spill Volume

Figure 16. Transportation materials balance flow chart.

flow rates (or quantities) geographically. Depending upon the spatial resolution desired, they may be distributed by regions or projected on a rather detailed grid. Data to establish this modal allocation can come from a variety of sources including transportation statistics developed at the federal or state level, transport company associations, and transortation companies, or the organizations that manufacture or distribute the product or chemical. In some cases it may be difficult to establish exactly the fraction of the chemical transported by truck or rail, or the distribution of the chemical in containers of different sizes. When data are lacking, production information as well as general knowledge of the properties of the chemical or product will help in achieving this modal allocation.

Development of Event Trees--

The next step in the analysis is the construction of an event-tree for each transportation mode of interest. In the case of a transportation mode, the event-tree is determined from the possible series of events leading to failures which could result in environmental releases. The releases may be either chronic (fugitive) or acute (spills). This analysis is a systematic procedure that starts with a "primary event" of interest, and then traces all possible combinations of circumstances that potentially lead to the primary event. The logical rigor imposed by such a procedure helps ensure that all assumptions are carefully stated in relationship to one another. Increasing the level of detail is straightforward because this generally involves an extension of the tree only at the last level of detail included, rather than at immediate points.

Event-trees have practical limitations. First, the development of event-trees is not a mechanical or automatic procedure. Detailed knowledge of the accident environment cannot be replaced by pure logic and anticipation. Second, it is possible for event-trees to be made so detailed that they lose all relevance. The end goal of an event-tree analysis must be a guiding principle when the level of desired detail is established.

Event-trees or diagrams are subdivided by system component, operations activity, and the nature of the release. For example, an event-tree for truck transportation might include the categories of loading, travel, idle time, and unloading. Releases within each category may be leakages of material characterized by fugitive loss factor such as vapor escape or by specific events leading to spills such as crushing, puncture and fire.

Estimation of Fugitive and Normal Releases--

Following the construction of an event-tree is the estimation of releases due to each occurrence. For fugitive losses, the vapor displacement during tank filling or the breathing loss in transit may be estimated using formulas which give the release as a function of the temperature and vapor pressure of the material. These are found, for example, in the standard handbook of air emissions inventory methodology (Compilation of Air Pollutant Emission Factors, U.S. Environmental Protection Agency, AP-42, August 1977).

Loading losses are the primary source of organic emissions from the vessel, tank car, and truck transportation operations. These releases occur as the vapors from the previous fluid loads residing in empty cargo tanks are displaced outward to the atmosphere by the liquid being loaded into the cargo tanks. The displaced vapors are a composite of those formed in the empty tank by the evaporation of residual product from previous hauls and those generated in the tank as the new product is being loaded. The quantity released from loading operations is, therefore, a function of the following parameters:

- method of unloading the previous material
- chemical and physical properties of the previous material
- method of introducing the new cargo
- chemical and physical properties of the new cargo.

Vessel ballasting operations are a major source of vapor losses associated with handling organic liquids at marine terminals. It is common practice for tankers to fill several cargo tanks with water after discharging the cargo to improve the stability of the empty ship while underway on subsequent voyages. These emissions take place as vapor-laden air and the empty tank is displaced to the atmosphere by the pumping of ballast water to stabilize the ship. In modern vessels, segregated ballast tanks are sometimes provided in order to mitigate this release loss.

An additional environmental release associated with transport operation is that occurring during transit itself. Small quantities of vapors are expelled from cargo tanks due to temperature and barometric pressure changes occurring during the transportation phase. Transient losses are calculated in terms of mass per unit time per unit volume transported and depend upon the vapor pressure of the transported liquid as well as density of the condensed vapors. Empirical formulas for estimating these losses are presented in the Compilation of Air Pollutant Emission Factors.

From the understanding of the mechanisms of these fugitive releases, the determination of the environmental compartments initially receiving these releases should be straightforward.

Accidental Releases--

Assessment of the releases due to spills or other accidents involves a casualty-based analysis involving the probability of spill for each individual event type and the size distribution of these spills. Associated with the spill estimate is an allocation by environmental compartment. This may be determined directly by the mode of release or by a specific methodology that differentiates among types of accidents.

There are two approaches available for estimating the probability and quantity of spills associated with various events. One approach uses stochastic modeling and the other employs empirical statistical methods. Because of the uncertainty associated with the modeling of accidents and failures, it is usually desirable to use actual casualty statistics. Exposure levels (such as total ton miles, total vehicle miles, volume flow rates, vessel years, or similar parameters) appropriate to the operation in question must be determined along with the total casualty experience for both the number of spills and their size distribution. These data are used in the standard methods of risk analysis by computing the exposure levels involved for the operation of interest in applying the spill frequency rate determined from historical information. The spill size distribution appropriate to the subset of events corresponding to these casualties then provides the information needed to generate a risk profile and to estimate the expected spillage.

Using the modeling approach, the frequency of occurrence and size distribution must be estimated. The frequency of occurrence is determined by simulating the operation and its potential failure modes that generate spill potential. The failure mode analysis combined with structural and fluid dynamics can be employed to provide approximations to the size distributions. These must be modified appropriately to account for mitigation measures that may be part of the standard operation. In the modeling approach, the quantity spilled may be related to the severity of the accident which has been the subject of an extensive analysis carried out by Clark et al. (1).

This study is presented in four volumes beginning with a summary, which contains the major results along with applicable examples. The other three volumes--pertaining to cargo aircraft, motor carriers, and trains--are engineering-oriented reports that detail the technicalities of the derivation of data and substantiation of the summary of results. The results include both the severities of accidents and frequencies of accidents since these two issues cannot be realistically addressed separately. The analysis is based on statistics of transport vehicles encountering accidents of different severities by physical models of the various consequences of an accident. Coupling these statistics and the analytical results, one can describe in a probabilistic manner the experience of a specific vehicle. The results can be stated as joint probability curves showing the probability per mile of exceeding some threshold value such as normal impact velocity or fire duration. The quantity spilled may be related to the severity with the aid of engineering models.

The severity parameter is a multi-dimensional variable made up of temperature/time exposure for fires, punctuate severity, and crush severity. The probability of experiencing a given number of accidents in each severity category as a function of transport miles is tabulated in the report mentioned above based on the Poisson approximation to the biomodal distribution to account for low occurrence rates per mile.

For spills into near shore or inland waters, the Pollution Incident Reporting System (PIRS) maintained by the U.S. Coast Guard, is a comprehensive source of casualty statistics. As mentioned above, the exposure level corresponding to these casualties must be determined independently. This system, which is computer based, has been maintained since 1971 for spills of all materials into U.S. waters and contiguous waters. Retrievals of casualty statistics can be made on descriptor set specifications involving location, rivers, states, outside of contiguous zones, water bodies, spill source, other transportation systems, cause (immediate and contributory), and type of material. An advantage of the use of this data base is that it reflects the level of control exercised in and near U.S. waters; furthermore, it is one of the most comprehensive efforts in the world to include all events occurring. As in all risk analyses, the use of this data source must be carefully coordinated with the exposure levels and casualty types so that conditions appropriate to the specific activity of interest are correctly represented.

Simplified Approach

The methods for estimating releases from transportation activities, both normal and abnormal, are probably more advanced than methods for estimating releases from other activities. Agencies such as the Department of Transportation, the U.S. Environmental Protection Agency, and the Nuclear Regulatory Commission have conducted a large number of studies related to accident and spill analysis that provide a reasonable statistical base upon which to estimate the nature and size of quantity of release from specific events. For most "initial level" materials balances, simple percentage estimates of possible releases during transportation, using release factors appropriate to each transportation mode, will probably suffice for placing the releases during transportation activities in perspective with other releases. If more detail is required, then a complete event and fault tree analysis, modeling studies or statistical data based approaches may be required. The common step in either a simplified or complex approach is to gain an understanding of the modal split of the product or chemical among transportation methods. Using the characteristics of the chemical or product and the general understanding of transportation methods, one can determine the environmental compartment associated with "typical" releases.

STORAGE ACTIVITIES

General Approach

Environmental releases of chemicals from storage activities are very similar to the materials balance for transportation activities. Since complete containment is a primary objective, fugitive and accidental losses again are the two main categories of release. Unlike the case of transportation, however, the storage-related losses are associated with stationary facilities. This means that the location of the releases may be well defined.

The objectives of the storage materials balance are to identify the locations and estimate the quantities of normal releases and to estimate releases of an abnormal nature via various statistical techniques. Normal releases are defined as those occurring during loading and unloading of the chemical from the facility, fugitive emissions during storage, losses during cleaning of the storage facility, etc. These releases depend on the type of equipment utilized, the chemical and physical properties of the material of interest and environmental factors such as temperature and pressure. Abnormal releases occur during accidents such as spills during transfer operations, tank ruptures, fires, explosions and leaks from improperly maintained equipment. Estimations of abnormal releases must come from probability distributions and construction of an event-tree.

For each individual event of a release from a storage facility the expected amount appearing in the environment is equal to the product of the probability of the event and the consequence, measured as the quantity released during the particular event. The materials balance in the aggregate is the summation of all of these expected values. From the point of view of fate and subsequent risk analysis, however, the aggregate releases are not as useful as the geographical and temporal distribution of various sizes of release. As in the case of transportation, the materials balance for storage must include both the normal emissions in either the liquid or the vapor phase and the entire spectrum of catastrophic events resulting in losses. As sub-events under the structural failure mode one can include all manner of possibility ranging from earthquakes to airplane crashes. Similar considerations must be invoked on the bin storage of solid granular materials with the added possibility of wind entrainment at open interfaces or fugitive loss points.

Specific Approach

The logical identification of the multiple causes for a single type of release is defined in an event-tree diagram (as discussed under the section dealing with transportation-related releases). Storage facilities have loading, unloading, maintenance, holding, and clean-out activities as possible classes of release modes. Within each activity, specific events such as mechanical failure, leakage, and explosion contribute as primary causes for these releases. One might identify factors such as operator error, vehicle collision, terrorism, vandalism, and wind storm as possible originating causes.

Either failure mode analysis or casualty statistics can establish both the frequency of occurrence and the size of the consequence (in the case of releases to the environment). A risk analysis of storage of hazardous chemicals prepared for the National Science Foundation by the University of California at Los Angeles (2), indicated the tank rupture was assumed to be 1×10^{-6} ruptures per tank year and the probability of a certain meteorological dispersion class simultaneously to be 5×10^{-2}. (A complete risk analysis would derive these figures either from modeling or from actual statistics.)

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Mitigation measures designed to minimize or to control the mode of release must also be considered in deriving the storage component of a materials balance. Containment of a liquid spill is normally provided by construction of dikes around storage tanks. This containment measure either permits recovery of some fraction of the spilled material or prevents the spread and subsequent leaching of the material or water contamination by the material. Thus the existence of diking changes the quantity or the distribution of materials released into the environment from a tank spill. Added features to the event-tree must be introduced in these cases to reflect the possibility of failure of the containment system. Dike breaching may occur because of the high momentum of the spill or because of simultaneous conditions that lead to dike failure. These simultaneous conditions may include undermining of the dike structure by erosion, previous damage to the dike structure by seismic activity, or over pressure failure of the dike structure due to associated explosions.

Fugitive losses associated with storage activities must be considered in computing a component of materials balance. The handbook of emissions inventory methodology (3) devotes an entire section to computing the losses from storage of petroleum liquids. Analogous methodologies can be applied to a variety of substances in the liquid phase by adapting different empirical coefficients to the expressions found there. In this reference, four basic tank designs are considered: fixed roof, floating roof (open type and covered type), variable vapor space, and pressure (low and high). Fixed roof tanks constitute the minimum acceptable method of storing volatile liquids. This design has been widely used in the past because it is usually the least expensive type to construct. Pressure/vacuum vents are standard design features in these tanks in order to contain minor changes in the vapor volume. Because of large exposed areas and relatively thin shell design, very small pressures of vacuum tolerance are acceptable for large fixed-roof tanks.

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The use of tanks with floating roofs reduces evaporative storage losses by minimizing available space for the formation of vapor. The roof rises and falls according to the depth of stored liquid and is equipped with a sliding seal fitting against the tank wall to insure complete coverage of the surface. Sliding seals are also provided where tank appurtenances such as support columns pass through the roof. Various types of floating roofs including the open-type, the pan-type, and the pontoon roof are the variations on the basic design to protect the roof deck from weather and to afford dirt protection for the sliding seal. One type of floating roof tank is essentially a fixed-roof tank with a floating deck inside the tank. A variation on this design is one providing for vapor recovery in the space between the fixed roof and the floating roof to intercept any evaporative losses brought about by the liquid film left behind when the roof descends and leakage that occurs around the wall seals.

Variable vapor space tanks may have a telescoping roof that fits in a liquid immersed seal, so that variability in the vapor space is achieved. There is also the possibility of using a flexible diaphram between the

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the liquid level and the top of the tank and equipping each sealed volume with pressure/vacuum vents.

Pressure tanks are used for the containment of high volatility materials and are closed systems designed for several pounds per square inch up to a few hundred pounds per square inch. These occur in many sizes and shapes, depending on the operating characteristics and withstand relatively large pressure variations to prevent losses.

Pressure tank losses, variable vapor space filling losses, floating roof withdrawal losses, floating roof standing storage losses, fixed roof working losses and fixed roof breathing losses constitute six sources of release from liquid storage tanks. When vapors expelled from a tank because of the thermal expansion of vapor in the headspace, vapor expansion caused by barometric pressure changes, or an increase in the amount of vapor due to continued phase change in the absence of a liquid-level change, fixed roof breathing losses will occur by expelling vapor through the tank vents. Working losses from fixed roof tanks consist of vapors released during the filling or emptying processes. When liquid is introduced into a fixed roof tank, the vapor that must be displaced outward is called a filling loss. Emptying losses are identified by the expulsion of vapors after the product is withdrawn. These losses are attributable to vapor growth as the stored material saturates the air that is drawn in.

Standing storage losses can result in floating roof tanks due to causes other than breathing or changes in liquid level. Imperfect fits of the seal to the shell exposing some liquid surface to the atmosphere constitutes the largest single potential source of this loss. Some vapor may escape between the flexible membrane seal and the tank roof also.

Withdrawal losses from floating roof tanks occur by phase changes from the film of liquid material wetting the tank wall as the roof descends during emptying operations. Compared with other losses, this one is relatively small.

Filling losses are defined as releases of vapor displaced by the liquid input during filling operations for variable vapor space tanks. Since the headspace vapor capacity is expandable, this loss is not as large as the filling loss associated with fixed-roof tanks. Theoretically, the only releases of vapor will occur when the storage capacity in the headspaces is exceeded.

Relief vents open on pressure tanks when the internal pressure exceeds the design or operating level. This loss occurs only when the tank is improperly filled or when abnormal conditions lead to vapor expansion. This is a casualty type and is not a significant source of loss under normal operating conditions.

The vapor losses from storage facilities depend both on the rate and the time period of interest. The factors that influence the loss rate include:

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- vapor pressure of the stored material
- temperature cycling in the facility
- headspace volume
- diameter of the tank
- time distribution of filling/emptying cycles
- the mechanical quality of the tank structure and associated seals
- the tank design and the qualities of the outside surface finish.

Several of these factors may not be readily identifiable, however. For liquid petroleum products storage, the American Petroleum Institute has developed a variety of empirical expressions relating losses to these factors. Formulas and working tables for loss estimates also appear in the Compilation of Air Pollutant Emission Factors.

Simplified Approach

Because data on losses from storage facilities may be limited, one may undertake a simplified analysis in order to identify these losses and generate an order-of-magnitude estimate for them. Other factors may also dictate the need for a simplified analysis. These may include time constraints, the minor role of storage losses in the overall materials balance or a very low level of risk associated with storage activities.

The simplified approach involves identifying the basic activities which result in releases. An example of a hypothetical materials balance for storage activities is presented in Figure 17. After identifying the loss mechanisms, one must estimate the releases associated with each. Assume that it has been determined or estimated that the following release factors apply to this case:

air: 5×10^{-6} grams/kg stored/year
water: 1×10^{-6} grams/kg stored/year

A review of the literature and input from previous activities in the materials balance indicate that 5 million metric tons are stored each year. This multiplication yields the following release estimates:

air: 25 kg/year
water: 2 kg/year

The equations presented previously coupled with data or estimates of the number of storage facilities, volumes/quantities involved and physical and chemical properties may also be employed in a simplified analysis.

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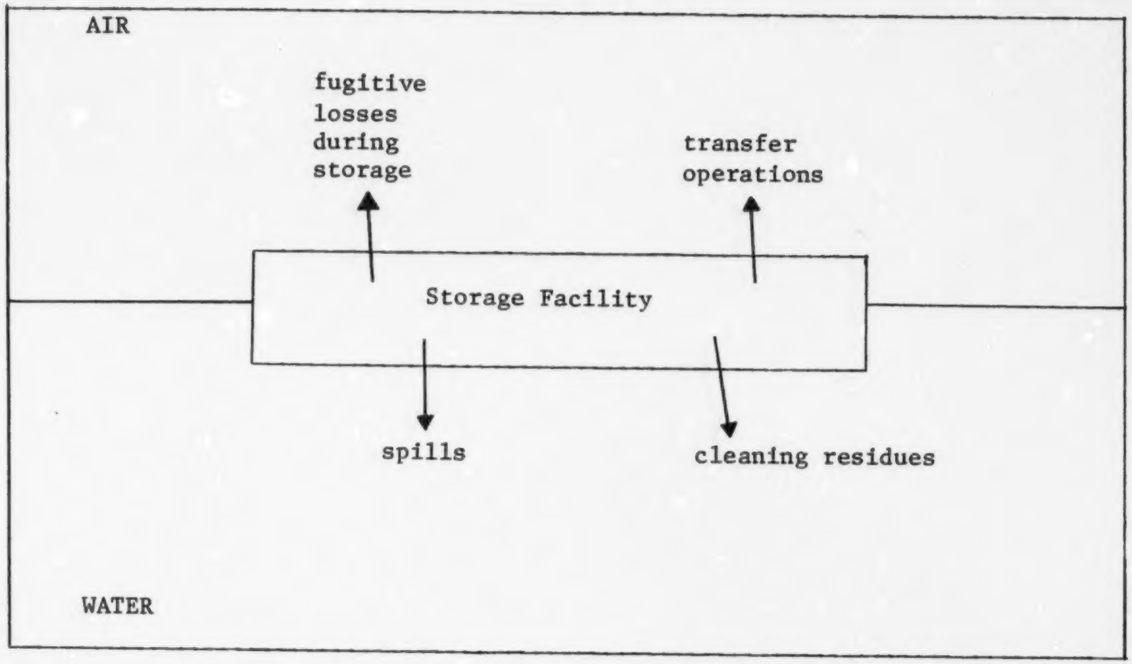
AIR
fugitive
losses
during
storage
transfer
operations
Storage Facility
spills
cleaning residues
WATER

Figure 17. Simplified materials balance analysis of storage activities.

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USE ACTIVITIES

General Approach

The purpose of refining and manufacture of chemicals and products is use. Use has come to mean the removal of a substance from its container or wrapping materials for distribution, application, or installation, usually with specific instructions concerning frequency and amount of use for systematic applications. These instructions form the basis of the "use pattern" which will enable a quantitative description of the use relevant to the range of products made from each chemical. These descriptions, on a "per use" basis, are useful for assessment of individual human exposure; on a gross annual scale, they should permit fate modeling to cover all relevant compartments with subsequent exposure analysis.

In performing the materials balance for chemical or product use, the amount of use, the location, and user are important to the final determination of both environmental fate and exposure. Therefore, they must be determined for the materials balance. As shown in Figure 18, several use categories, based on land use and census data considerations are included: domestic, institutional, commercial, industrial and agricultural use. Uses may be considered to be consumptive, confined, distributed and applied. Consumptive use involves a chemical alteration of the material. Confined use refers to materials which remain enclosed during their lifetime, such as refrigerants in a refrigerator. Distributed use involved products such as pesticides that, during their normal use, become dispersed throughout the environment. Applied use involves no chemical changes such as paints. Three environmental compartments for discharges or emissions--land, air and water--should be considered for each use.

The steps of the procedure are shown in Figure 19. Simply, the process involves identification of the various products (they may be specific chemicals or products containing the chemicals), development of a qualitative description of the products use and users, quantitative analysis of products usage and release rates to generate the amounts released to each compartment.

Specific Approach

In Table 4 the input sources and outputs necessary to each step in the materials balance procedure are given. Following detailed explanations for each step, a sample calculation is shown.

General Product Identification--

The initial information base for product use comes from the output of the materials balance results for manufacturing activity. This information will be in the form: q_i metric tons per year of product x_i where i represents any generic product or product group made from or including the chemical under analysis. The generic description does not have to include

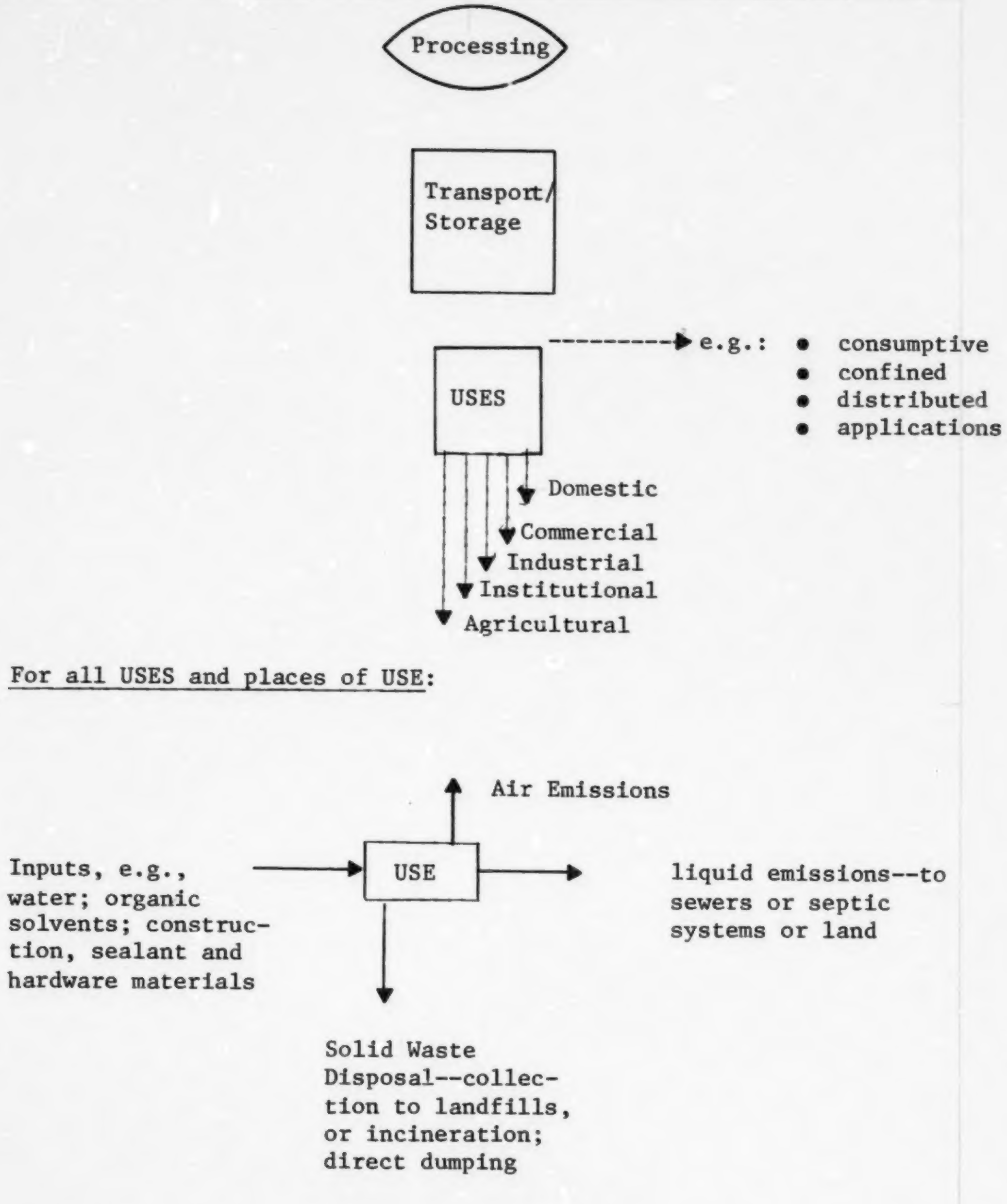
Processing
Transport/
Storage
USES
e.g.:
• consumptive
• confined
• distributed
• applications
Domestic
Commercial
Industrial
Institutional
Agricultural
For all USES and places of USE:
Air Emissions
Inputs, e.g., water; organic solvents; construction, sealant and hardware materials
USE
liquid emissions--to sewers or septic systems or land
Solid Waste Disposal--collection to landfills, or incineration; direct dumping

Figure 18. Use activities--materials flows.

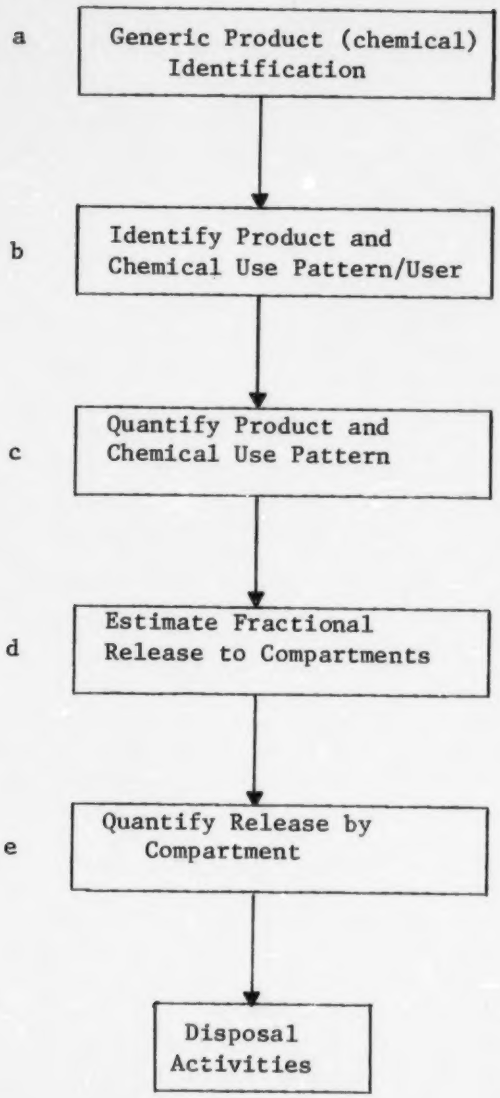
a
Generic Product (chemical) Identification
b
Identify Product and Chemical Use Pattern/User
c
Quantify Product and Chemical Use Pattern
d
Estimate Fractional Release to Compartments
e
Quantify Release by Compartment
Disposal Activities

Figure 19. Procedures for use activities materials balance.

TABLE 4. USE ACTIVITIES--INPUT SOURCES AND OUTPUTS TO MATERIALS BALANCE PROCEDURES

a.	Generic Product and Chemical Identification 1. Input Sources: Output from Manufacturing and Processing Activities Materials Balances 2. Outputs: Quantified Chemical or Product List, Percent Composition
b.	Identify Product and Chemical Use and Use Pattern/User 1. Input Sources: Manufacturers, Commerce and Agriculture and Census Data 2. Outputs: User List by Type and Number, Place of Use, Form of Product or Chemical During Use
c.	Product and Chemical Use Pattern Quantification 1. Input Sources: Manufacturers, Consumer Groups, etc. 2. Outputs: Release Rates by Compartment, Including Product Lifetimes
d.	Compartmental Release Fractions 1. Input Sources: Chemical and Physical Properties 2. Outputs: Amounts and Fractions of Product or Chemical Released by Compartment
e.	Release Quantification by Compartment 1. Input Sources: Above 2. Outputs: Quantities of Chemical Released into Each Compartment

brand names, but may give an idea of the proposed use of the product. The percentage of the chemical of concern which is present in the final product is also data obtained from the previous steps. Because production quantities are often not available by company, the data must be aggregated for the industry as a whole, either from trade organizations or government agencies, such as the Departments of Commerce and Agriculture, Bureau of Mines, Food and Drug Administration, and EPA, and the literature. Sources at state as well as regional and national levels should not be overlooked. Wherever possible, a geographic distribution of use should also be made.

Similarly, manufacturers may be reluctant to reveal percentage of specific chemicals in their products. Trade journals are often revealing, as are chemical engineering process descriptions. Product sampling and analysis data may be available from the sources mentioned above as well as in published literature. If not, rough estimates will have to be made.

Identify Product Use--

The generic descriptions should be expanded to include information which will clearly identify the users of the products and the forms and the places in which they are used.

- Users should be distinguished by the terms: domestic, commercial, institutional, agricultural, industrial, etc. This is because although some products, disinfectants, for example, may be used in all places (except agricultural) the frequency of application and product formulation may vary with the user as will the amount that enters an environmental compartment.

- Places of use should be as specific as possible, for instance, domestic gardens, industrial floor cleaning, commercial cooling systems, etc.

- Because the physical form of the material at the time of its use is critical in determination of its release to the environment, the amounts used or applied in gaseous, liquid, dissolved or solid, etc., forms should be established.

Most of these data can be obtained from the companies which make the various products. The manufacturers can supply descriptions of the intended purpose and form of each relevant product, which would be useful in identifying or assuming the likely user groups and places of product utilization. The numbers of users or user groups may be estimated from the United States Census Data; for example, numbers of households for domestic use.

Quantify Produce Use Patterns--

Once the types of uses and use patterns are identified, the amounts of the material used for all its purposes and release rates for these uses, based on product lifetime and use patterns, must be determined. Necessary data for each product or chemical are:

- The amount involved during each individual use of the product
- Frequency of use
- Duration (time period) for each use
- Quantified use of other materials (substances) during or after (clean up) use such as applicators, toweling, etc. (This will be input to disposal materials balance.)
- "Shelf Life" of the product (meaning time period up to which product is usable and will then be dispersed)
- Percent consumed before disposal--or how much cannot be extracted from the container prior to disposal.

These data will provide an overview of environmental releases of each product: release rates, in mass/time can be quantified in practical units such as grams/day for use by an individual homeowner or metric tons/year for aggregate user groups. Ideally, the release rate would be determined as the amount involved per use and accompanied by an estimation of the number of uses in a year, as this allows the most accurate calculation of exposure levels. This is also an approach to calculate total amount used per annum. Alternatively, the annual production is often used to estimate annual use.

Such information is often available from the manufacturers themselves; some can be obtained from consumer survey and consumer protection groups; some will be common sense observation. Where detailed data on a per use basis are not available, then aggregation of all the chemicals as products must be done. Additional information sources are government agencies relevant to the type of chemical of concern.

Estimate Practical Release to Compartments--

With the use of data collected in the last two steps, the amounts of the products which are released to each environmental compartment at the time of their use can be estimated. Some information on physical properties of the components of the product may be necessary for these analyses. For each product the following question must be answered. What fraction of the product is released (accidentally or purposely) into each environmental compartment during its use? Combining the information on use pattern, physical form and physical properties of the product, the quantity of any product or chemical that is used can be partitioned into environmental compartments or noted as a residual quantity for disposal, storage, etc. The description of the use pattern should include other materials used in preparation, clean up or during the use of the product. Some amount of the product may be associated with these materials, and they should be included. These calculations are relatively simple: the release rates for each product (from Step c) are multiplied by the partitioning factors determined above to derive amounts of the product released into each compartment over the period of time represented by the release rate--kg/year, mg/sec, etc. The releases by compartment should be reported on a consistent basis, e.g., the amount per year per compartment for comparison purposes. If the chemical is applied to land, the amount per year per unit area will be the desired form of the release. Similar judgment must be used for each chemical considered.

Quantify Release by Compartment--

Using the concentration of the pollutant in each product or chemical, and the amounts released by compartment per product, the quantities of the pollutant released to each compartment are determined. The totals released per unit of time are meaningful for environmental fate calculations. Note that the time scales may vary with the compartment, as a function of the pollutant's chemical properties. Finally, the annual pollutant releases for all products are summed for all compartments.

Example--

This example was taken from the risk assessment for phthalate esters being performed by Arthur D. Little, Inc. for the EPA. In this case much of the analysis was the result of in-house expertise, especially the assumption of certain release rates and proportions.

Some of the many generic products made with di-2-ethylhexyl phthalate (DEHP) are shown in Table 5, along with the fraction which each product represents of the total United States supply of DEHP.

The example will focus on one use of DHEP: use in vinyl flooring, which represents 22.6% of its use category.

The use pattern for flooring involves a lifetime, estimated to be 10 years, of contact with the air in domestic, industrial and commercial establishments. During its lifetime, the flooring will be washed with detergents and is exposed to the air on one face. In our study, variables such as the solubility of the plasticizer (i.e., DEHP) in the particular detergent, the transfer from the flooring into the detergent as well as the frequency of washing and the amount of wear of the floor were not evaluated, and they will not be considered here. The annual release rate from the floor to the air was assumed to be 0.002% of total DEHP present, a conservative estimate based on data.

Annually, 369.2×10^6 pounds of DEHP are made; 71.28×10^6 pounds are made into flooring. Applying the release rate to air (0.002%), it is determined that 142,600 pounds are released annually from flooring uses.

TABLE 5. A MATERIALS FLOW FOR DEHP

Total Production, in millions of pounds		369.2
Use Categories	Fraction of Total Production in This Use	Amount in Product
Other Polymers	.05	16.99
Plasticizers		
• Swimming pool liners	0.14	4.56
• Garden hoses	.01	3.26
• Medical uses	.11	35.89
• Flooring	.226	71.2
• Weather stripping	.015	4.73
• Furniture	.112	35.29
• Wall covering	.040	12.6
• Auto mats and tops	.033	10.39
• Auto upholstery	.112	35.29
• Apparel	.100	31.5
• Food wrap	.015	4.73
• Wire and cable	.183	59.71
• Housewares	.038	12.39
• Sport goods and toys	.043	14.03
• Other PVC uses	.045	14.68

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Thus, over the 10-year product lifetime, 1.43 million pounds of DEHP are released to the air from a year's production of vinyl flooring. The remaining DEHP, 69.95×10^7 pounds, is disposed after 10 years. If transfer rates are available for the DEHP which moves from the flooring to washwater, they should be utilized. This would include solid and liquid DEHP.

Simplified Approach

The materials balance described above, may be considerably simplified if time and other constraints, including a scarcity of data, point to this approach.

Instead of summing the results of product-by-product analysis, products should be grouped by general use pattern and release rates for each compartment estimated by group. Releases by compartment may then be estimated as a percentage of manufacture or sales for each group. This approach can significantly reduce accuracy and does not provide the same detail for exposure analysis possible with the longer method.

Discussion

By going directly to manufacturers for use pattern and product composition data, accuracy and certainty are maximized. Performing the complete materials balance for use activities will be highly labor intensive and will be a function of the extent of use of the pollutant. Source identification is an outcome of this approach, and it will therefore be simple to identify possible controls.

The analysis is flexible in that surrogate chemicals may be used without losses in accuracy or certainty, and scale changes may be made in a simple, straightforward manner. Monitoring data are not generally appropriate due to the complexity of possible sources in a given area.

DISPOSAL ACTIVITIES

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General Approach

Disposal may be regarded as the process of removing materials which have no further utilization potential (or those which it is as yet not cost effective to recycle) from the cultural environment. By means of the Resource Recovery and Conservation Act, the type and location of disposal sites have been restricted for protection of the human and biotic environment.

The material balance procedure for disposal activities is designed to quantify the major disposal flows shown in Figure 20. Disposal results from extraction, refining, manufacturing, processing and use, with potential disposal from transportation and storage, e.g., containers. It is important in the materials balance to avoid double accounting in different activities. Thus, although inputs other than manufacturing, process wastes and uses could be shown in Figure 20, our discussion will focus on these three areas for disposal.

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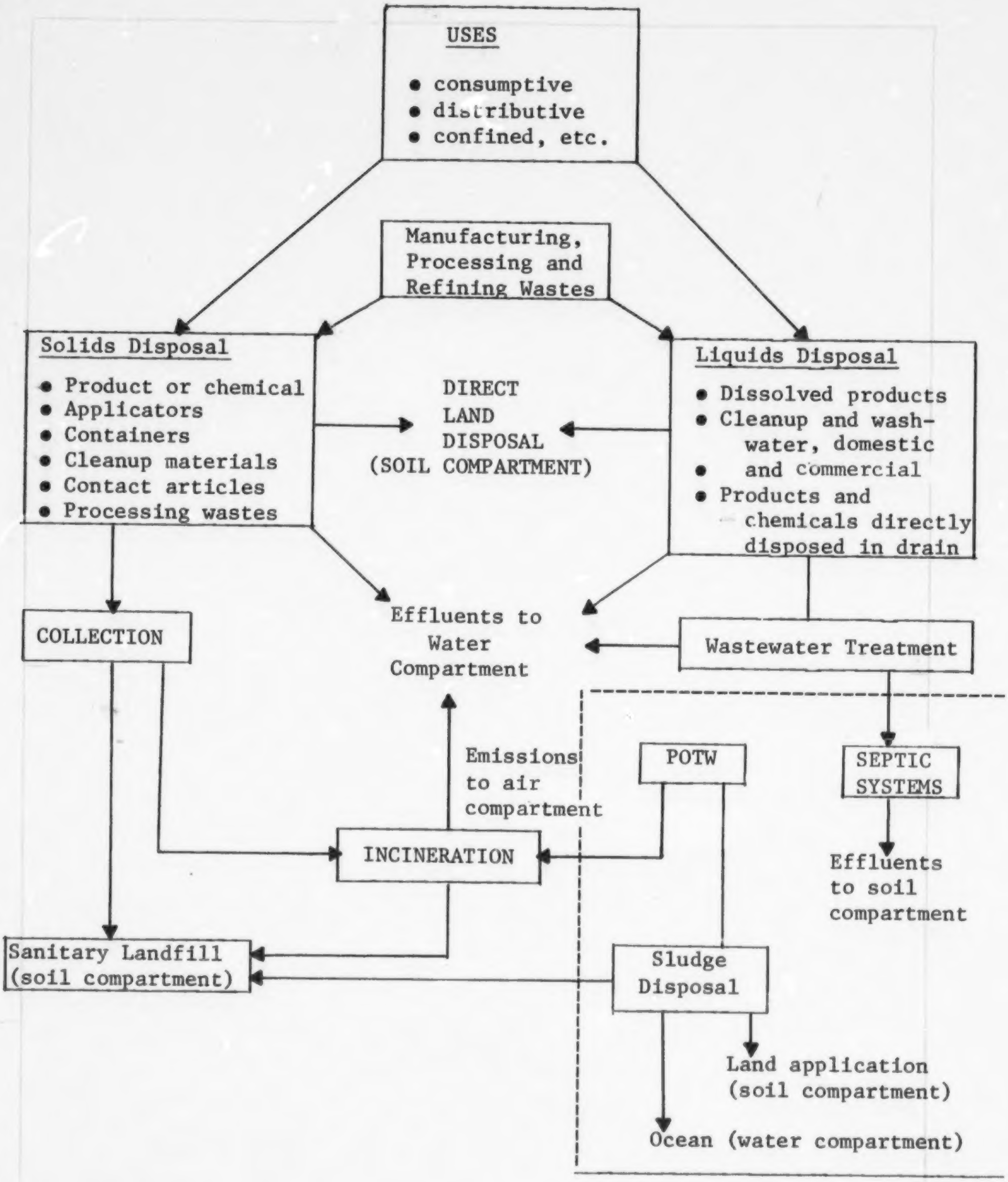
USES
• consumptive
• distributive
• confined, etc.
Manufacturing, Processing and Refining Wastes
Solids Disposal
• Product or chemical
• Applicators
• Containers
• Cleanup materials
• Contact articles
• Processing wastes
DIRECT LAND DISPOSAL (SOIL COMPARTMENT)
Liquids Disposal
• Dissolved products
• Cleanup and wash-water, domestic and commercial
• Products and chemicals directly disposed in drain
COLLECTION
Effluents to Water Compartment
Wastewater Treatment
Emissions to air compartment
POTW
SEPTIC SYSTEMS
INCINERATION
Effluents to soil compartment
Sanitary Landfill (soil compartment)
Sludge Disposal
Land application (soil compartment)
Ocean (water compartment)

Figure 20. Disposal activities--material flow.

The total disposal flow is categorized as solid and liquid flows. Solid flows include the specific chemicals or products (e.g., zinc metal, zinc chloride, or galvanized metal), chemical or product containers (e.g., spray cans) and packaging materials, applicators (brushes, fabric), clean-up materials containing the residual chemical (e.g., sponges, absorbents, etc.), contact materials--those items which the chemical or product was specifically meant to contact, such as painted articles, items sprayed with pesticides, and confining items, such as compressors containing chemicals and products in liquid form, those meant to be dissolved upon use (e.g., photographic chemicals, soaps, etc.), those disposed in municipal or private sewers or septic systems (e.g., solvents, thinners) and the quantities washed from users, application equipment, home and garden runoff, etc., following use. Note that there may not be a clear separation between use and disposal as in the case of soaps, thinners, or other chemicals used in cleaning and disposal operations.

In outlining this methodology, we have focused on "organized" solids collection from municipal and industrial sources, with sanitary landfill disposal or incineration as the mechanism of disposal for the bulk of the country's solid waste, neglecting those wastes which might be disposed of on private land by individuals, e.g., farm dump sites, etc. The liquid wastes we considered include inflows to wastewater treatment plants from industrial as well as domestic sources. Because waste recycling and processing (into fuel for example) is still an infant industry for most chemicals and products, this aspect has also been omitted from consideration. Future shifts in the economy may alter the importance of these disposal streams and they should then be examined.

Disposal through wastewater treatment plants (POTWs) and individual septic systems should be included. The level of quantification to be achieved in this materials balance segment will depend on the nature of the data available for a specific pollutant, its accuracy and extent. Direct disposal to air is omitted from this analysis because it is considered under other activities previously described. Such disposal takes the form of stack gas emissions, storage and transportation tank venting, stack gas flaring, etc.

A procedural flow sheet which summarizes the major steps in performing this materials balance is given in Figure 21. This procedure depends on a thorough identification of amounts of chemicals and products which are disposed, consciously or otherwise. Four disposal flows, direct-to-land (landfills and dumping), direct-to-water, POTW or septic systems, and incineration should be identified and quantified. There are two disposal processes which can chemically alter a material and therefore remove it from the waste stream: wastewater treatment and incineration. These changes must be considered on an individual chemical basis by examining chemical or physical changes possible, based on the properties of the material.

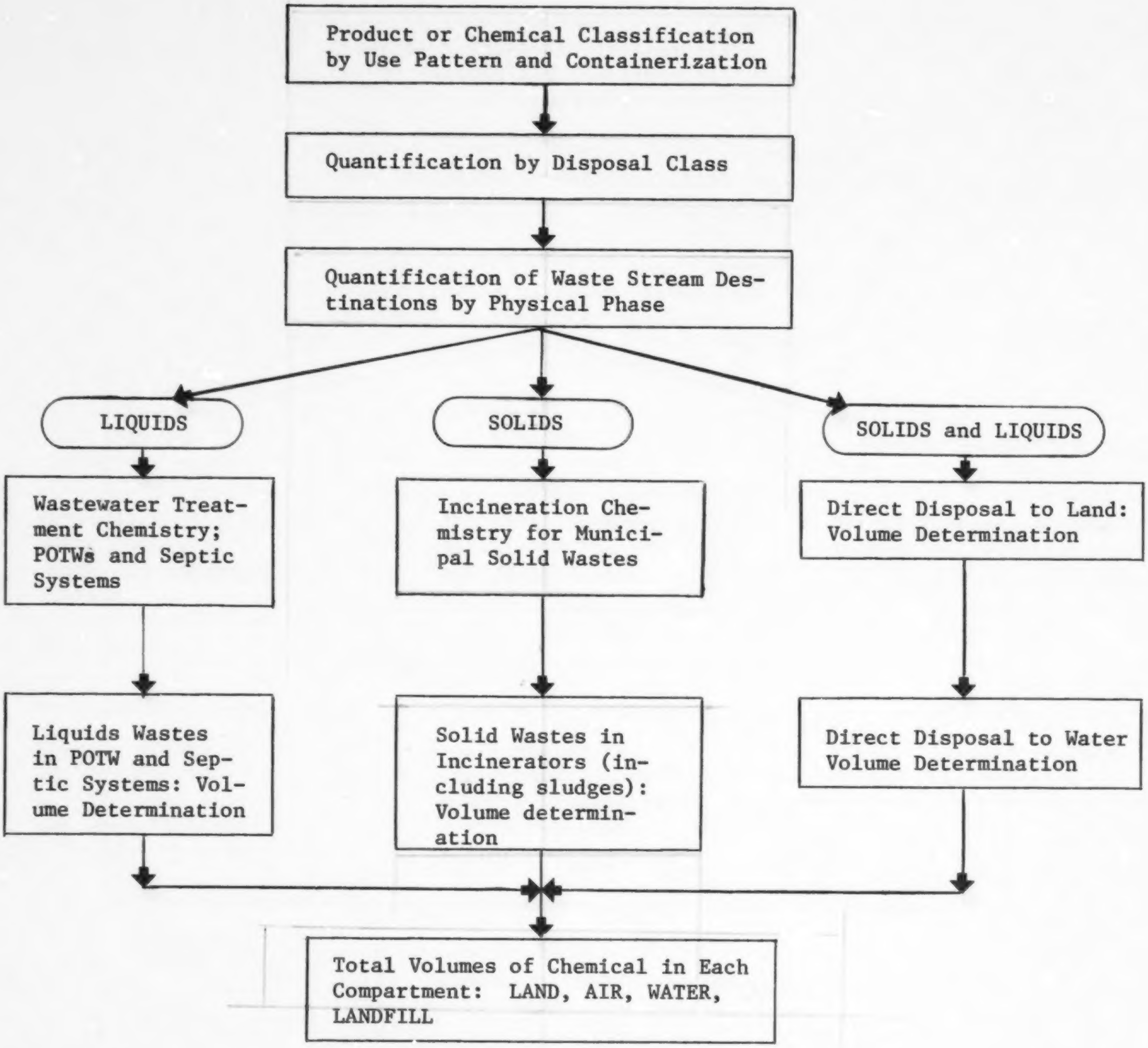
Product or Chemical Classification by Use Pattern and Containerization
Quantification by Disposal Class
Quantification of Waste Stream Destinations by Physical Phase
LIQUIDS
SOLIDS
SOLIDS and LIQUIDS
Wastewater Treatment Chemistry; POTWs and Septic Systems
Incineration Chemistry for Municipal Solid Wastes
Direct Disposal to Land: Volume Determination
Liquids Wastes in POTW and Septic Systems: Volume Determination
Solid Wastes in Incinerators (including sludges): Volume determination
Direct Disposal to Water Volume Determination
Total Volumes of Chemical in Each Compartment: LAND, AIR, WATER, LANDFILL

Figure 21. Procedures for disposal activities materials balance.

Specific Approach

Table 6 details the key sources for data inputs and lists the specific outputs of each step in the procedure. The steps are described below and the entire procedure is followed by an example.

Product Classification--

The various products described in the "use" activities of the materials balance (as well as manufacturing or process wastes) should be classified according to the following criteria:

(1) container type
(2) use pattern, including lifetimes and shelf life
(3) utilization of other materials which contact the product; applicators, clean-up supplies, articles meant for contact, e.g., painted surfaces.

A chemical or product may belong in one or all categories, the number of which will vary with the pollutant. The purpose of classification is to thoroughly document all possible routes by which the pollutant can be disposed.

The data developed in the previous materials balance segments may have to be amplified for this classification process.

- Container types include: spray or other containers which may or may not be completely emptied of their contents; containers which may be emptied but contain residues such as paper, plastic, cardboard or metal packaging materials, which are often put to other uses, etc.

- Use pattern data should incorporate sufficient information to calculate the amount of chemical or product in each use, the time frame of use, the time period between uses (or the time to use up one packaged unit) and the number of uses per packaged unit. The description of the product's use pattern must provide sufficient detail to determine if the product is sprayed, dissolved, painted on, placed someplace, heated, etc. Any information which will aid calculation of losses due to physical properties of the substance is relevant (for example, vaporization).

- Use of other materials during application is usually apparent from the instruction for product use. Many products (paints, insecticides, etc.) come with a manufacturer's estimate of the area which it will physically cover.

TABLE 6. DISPOSAL ACTIVITIES--INPUT SOURCES AND OUTPUTS TO MATERIALS BALANCE PROCEDURES

a. Product or Chemical Classification by Use Pattern and Containers

1. Input Sources: Outputs from "USE" Materials Balance
2. Outputs: Container types, use forms, and contact materials lists

b. Quantify by Disposal Class

1. Input Sources: "Use" data, manufacturers, consumer groups, literature
2. Outputs: Quantities of chemical in each class

c. Quantify Waste Streams Destinations

1. Input Sources: Use pattern
2. Outputs: Volume of chemical collected or disposed as solids, liquids (sewage and septic waste), liquids dumped

d-1. Wastewater Chemistry: POTWs and Septic Systems

1. Input Sources: Physical and chemical properties from literature
2. Outputs: Percentages of the chemical inflow which are: destroyed, volatilized, in sludge, and in effluent

d-2. Liquid Wastes in POTW and Septic Systems - Volume Destination

1. Input Sources: Municipal and State Agency data, above analysis
2. Outputs: Amounts of effluent, sludge disposed by land, landfill, incineration, ocean, number of septic systems and the volume of chemical in each flow

e-1. Incineration Chemistry for Municipal Wastes

1. Input Sources: Literature, physical and chemical properties
2. Outputs: Percentages of the chemical inflow which are: destroyed, volatilized, on particulates, in the ash

e-2. Solid Wastes in Incinerators - Volume Determination

1. Input Sources: Municipal and State Agency data, above analysis, stack emissions control device efficiency
2. Outputs: Amounts of the chemical emitted to the air and buried in landfills as ash

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TABLE 6 (Continued)

f. Liquids and Solids Directly Disposed to Land and Water-Volume Determination

1. Input Sources: Use Pattern
2. Outputs: Quantities of the chemical directly released in solid and liquid forms to land (soil) and water

g. Total Volumes of Chemical in Each Compartment

1. Input Sources: above analysis
2. Outputs: Quantities of the chemical in land (soil), landfill (sea), water and air

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Disposal Class Quantification--

Using the classification list developed in Step a, the quantity of products or chemicals belonging in each group must be determined. Then the actual amount of each product which is disposed in each group must be estimated. The compositions of each product (from "USE" analysis) can be multiplied by the amount disposed per product per group to obtain quantities of the chemical disposed. In some cases, because of data gaps or variability in individual consumer practices, common sense estimates may be required. This will be especially true in the case of container residues and application and clean-up materials and practices. Consumer groups may prove useful in providing some of these data.

Waste Stream Destinations--

The amounts of the chemical disposed, determined in Step b, and next regrouped according to their final destination: the solids collection and disposal route, the domestic septic tank or, via sewers to the POTW and direct releases to land and to water bodies. For simplicity, it can be assumed that those wastes which are incinerated are a fraction of total collected solid waste, based on the total capacity of all the nation's municipal incinerators. The wastes which are released directly to water will include both solids and liquids and these amounts must be estimated as some proportion of the total waste amount. Similarly, liquid waste volumes which are treated in septic tanks as opposed to POTWs probably represent some fraction of the total wastewater stream. A distribution between these two treatment methods must be assumed.

Manufacturing, processing and other wastes are often inputs to POTWs or municipal landfills. Adding the amounts quantified in the previous materials balance analyses as wastes from these processes, the total volume of the chemical in each waste stream is calculated. Each stream can then be analyzed separately for its ultimate fate.

Liquid Waste Stream Analysis--

Wastewater treatment process chemistry--If the chemical has an existing or potential disposal route in wastewater, either in POTWs or in septic tanks, the physical and chemical processes used in treatment must be analyzed with respect to fate of the pollutant. An estimation of percentages destroyed (hydrolysis, reduction, etc.), volatilized, sedimented, bioaccumulated, etc., will provide an overall figure for the proportions which are in the final sludges and effluents. Some care must be given to examine synergistic effects--especially if industrial wastes are involved. Literature is the best source for this analysis either in journals or EPA publications and will be pollutant specific.

Disposal volumes from wastewater sludges and effluents--While each individual waste treatment plant, public or private, disposes of its wastes in a different way, statistics obtained from state and federal agencies can provide an overall picture of the proportional destinations of sludge and effluents. Many POTWs also receive and treat septic tank contents. Some sludges are dried and buried in landfills; some are incinerated, some are used for fertilizer and applied to land, and some are discharged to bodies of water. Most effluents are released to flowing water although some are sprayed on land for a final treatment step. The present distribution of wastes may be used for all chemicals which reach the sewer system.

In septic tank analysis, the effluent volume will be equal to daily inflows once steady state has been reached. Assuming average uses of the products per household, and using this factor multiplied by the estimated number of septic systems, a total chemical flow may be estimated. Data on the number of septic systems may be available from EPA as the result of 201 planning.

Combining the information on chemical reactions from these steps with the physical destination proportions determined above, the amounts of the chemical under analysis which are part of the various disposal scenarios described may be determined. The volumes of chemical which are in effluents, buried, incinerated and fertilizer sludge, and septic systems are the outputs of this step.

Solid Waste Stream Analysis--

Incineration process chemistry--The combustive properties of the chemical in incinerators must be considered. This may consist of literature review, laboratory tests and analysis of the properties of the pollutant in its various states and analysis of the properties of the pollutants in its various products. The analysis should provide estimates for the percentages of incoming chemicals which are: destroyed, volatilized, associated with particulates, associated with the ash residue by incineration. Using these percentages, the flow of the incoming volume of toxic chemicals can be quantitatively broken down into ash constituents and stack gas constituents, less the amounts destroyed.

Disposal volumes from incineration--Incinerators usually have particulate emissions controls. Based on municipal and EPA data, it should be possible to estimate an average operating particular removal efficiency of the various installed precipitators. Applying this efficiency to the stack gas associated amount of pollutant allows the determination of the actual quantities of the pollutant destined for landfill burial and for atmospheric loss.

Solid and Liquid Waste Streams--

Some proportion of a given chemical or product will be disposed of in solid or liquid form without treatment and received directly by land or water.

Land--Direct disposal to land includes sanitary landfill operations, runoff, spreading and dumping. These proportions, other than the landfilled fraction, are exceedingly difficult to quantify, and estimations will have to suffice in most cases.

Water--Water disposal consists of untreated industrial domestic or commercial discharges. These include deliberate dumping of materials by individuals. As above, estimations will be relied upon to quantify this process.

Final Destination by Compartment--

With the data gathered and analyzed in Steps c, d-2, e-2, and f, the total volumes of the pollutant which reach the three environmental compartments--land (sanitary landfill, sludge or effluent application, direct disposal), water (direct, sludge and effluent discharges) and air (incinerator emissions) may be summed. Depending upon data availability, and how the analysis is carried out, the results may include time and geographic location as factors. (This analysis does not include movement from the original disposal destination, i.e., from landfills to air or water. This would be the subject of environmental fate analysis.)

Example--

We have not identified in the literature analyses which completely follow the procedure outlined above, although several studies have used parts of it.

A materials balance analysis, conducted by Arthur D. Little, Inc., for EPA on phthalate esters assumes that at the end of a product's lifetime all of the manufactured quantity is disposed. The amount of chemical which is disposed is that which remains in the product at the time of disposal.

For the chemical di-2-ethylhexyl phthalate (DEHP), used in polymers, the following materials balance was determined (all figures refer to the year 1977):

- 18.42×10^{6} pound manufactured
- 20,000 pounds lost during transportation
- 533,000 pounds vaporized (lost to air) during compounding
- 894,000 pounds were included in manufacturing wastes
- No polymer-DEHP is lost during use
- All polymer-DEHP put to use is eventually disposed
- Total volume disposed to land use was estimated at 97% of total used (16.48×10^{6} pounds) plus manufacturing waste (894,000) or 17.34×10^{6} pounds disposed
- It was assumed that DEHP was evenly distributed throughout collected solid wastes. The incinerated fraction of collected solid wastes was estimated to be 3% of the total disposed volume. Therefore 510,000 pounds was incinerated. The fractions lost to air and returned as ash to the landfill were not documented.

Simplified Approach

Where factors of time, budget and staffing constrain a complete disposal materials balance approach, the following simplifications can be made to disposal in the interest of establishing at least a "ball park" materials balance.

Using the chemical's product usage figures, and by examining the kinds of uses, one can estimate a gross disposal based on material properties, containerization, etc. This figure may again be crudely split, according to use pattern, into solid and liquid disposal streams. It should be stressed, however, that once the proportions of incinerated vs. buried solid waste and incinerated vs. "other disposal" for wastewater sludge have been determined, these factors can be applied to all simplified analyses, so determining these fractions may be worth the extra time involved. It has been estimated that 60% of sludge is disposed on land, 10% ocean dumped and 30% incinerated (4), and that 2% of municipal waste is incinerated (Lamb, personal communication). These figures may be used in lieu of further research if time and other constraints are pressing. The physical/chemical fate of each individual chemical will naturally be unique during incineration and wastewater treatment. There are no shortcuts to analyzing these processes. The only possibility is that the chemical under study may resemble another chemical whose behavior in these circumstances is known and understood.

Such an approach will reduce the accuracy of the analysis and will also limit the estimation of exposure possible from intensive use pattern procedures.

Discussion

Using the detailed materials balance procedure, the user should be able to clearly document the uncertainty levels and assumptions made in the analysis. Given a specific chemical, some consultation with EPA on data availability and knowledge of the industrial climate will allow some estimate of time, human resources, confidentiality of monitoring data, scale and resolution to be made, which will indicate whether specific or simplified approaches should be used.

This materials balance procedure can be quite time consuming if great detail is desired, particularly if consumer products are considered. The greater the detail, however, the greater the accuracy. As noted, the simplified approach will reduce the confidence of the results. The process is sufficiently thorough to allow significant potential environmental impacts at various points on the waste stream flow to be identified for future study.

The methodology described is comprehensive and oriented to achieving maximum accuracy in the exposure and fate assessment which will follow. POTWs and sanitary landfills can be considered as source controls. Through the materials balance, it can be determined if other controls for more direct disposal routes are possible.

NATURAL SOURCES

As indicated in previous sections, a complete materials balance must include the contributions of natural sources of toxic pollutants to the environment as well as those sources that are anthropogenic. Natural sources cannot really be considered as a separate "activity" in the development of a materials balance, but the inputs of pollutants from the natural environment to various cultural activities must be examined and placed in perspective with the inputs of pollutants generated by those cultural activities. Therefore, in formulating a materials balance for a toxic pollutant, several questions related to natural sources must be addressed :

- What are the sources, the quantities generated, and the locations of entry of the toxic pollutant to the environment?
- How much of these naturally derived toxic pollutants enter the cultural environment and under what conditions or at what locations?
- How much of the toxic pollutant found in the environment is derived from natural sources?

No single comprehensive methodology for evaluating the contributions of natural sources of toxic pollutants to a materials balance exists because of several factors: (a) it is often not clear whether or not many toxic pollutants are a result of natural processes or man-made sources; (b) there may be many different types of natural sources for some few toxic pollutants; (c) data on concentrations or amounts of naturally derived toxic pollutants in the environment are not readily available; (d) the interfaces between natural sources and flows into the cultural environment are not clear (e.g., mining of minerals, concentration of metals or pollutants in food crops, runoff of sulfate particulates derived from natural sources, etc.). As a result, natural sources will have to be considered somewhat independently in the formulation and conduct of a materials balance. In the paragraphs which follow, we will discuss some general considerations and approaches to answering the questions posed above.

There are a number of different types of toxic pollutants that may result from natural processes. These include: metals; metal oxides, sulfides, sulfates, carbonates, halides and other metallic salts; alkali metals and salts; organic and inorganic sulfur compounds, organic and inorganic nitrogen compounds; petroleum or coal derived hydrocarbons; and simple and more complex organic chemicals. Although there is general agreement that a large number of complex organic compounds result only from anthropogenic sources, there is speculation and growing evidence that some complex organics, e.g., dioxins, nitrosoamines, etc., can result from plant or animal metabolism, degradation, or natural combustion processes. Therefore, in conducting a materials balance for a specific toxic pollutant, one should not a priori discount natural sources without some literature research on the production of the pollutant via naturally occurring processes.

Natural sources of toxic pollutants can be considered as historic or contemporary (passive or active) in their generation/origin and release. For example, petroleum and its chemical components are historic in origin but contemporary in release through oil seeps, shale outcrop erosion, etc., whereas hydrogen sulfide is contemporary in its generation and release by sulfate reducing bacteria in swamps or mud flats. Table 7 lists several types of natural sources of toxic pollutants classified according to their origin or generation.

TABLE 7. POSSIBLE NATURAL SOURCES OF TOXIC POLLUTANTS

Historic	Contemporary
Metals, mineral and ore deposits	Soils--erosion and runoff
Petroleum deposits--reservoirs, shales, sands	Biota--natural vegetation (trees, fruits, grasses)
Coal, lignite, peat deposits	--natural biodegradation (microbial or bacterial decay in soils, swamps, lakes, lagoons, sediments, etc.)
Sulfur, salt deposits	--algal growth and decay
Limestone, sandstone, shellfish deposits	--animal growth, metabolism, decay processes
	Volcanic activity
	Natural combustion--forest fires
	Formation in upper atmosphere
	Lightning

In conducting a materials balance for a specific toxic chemical, one should consider each of these as potential sources, rapidly eliminate those which are not feasible, and proceed through literature research or discussions with recognized experts to determine, quantitatively if possible, the magnitude (and location) of possible natural environmental releases.

The next step would be to determine where any toxic pollutant derived from natural sources are used in the cultural environment. For example, metals enter directly from mining or extraction processes, but they can also enter from agricultural runoff, erosion of soils, urban runoff, etc. Certain inorganics such as sulfate particles may enter through dry deposition and urban runoff; organics may enter through the foodchain. It will be important in conducting the materials balance to separate those toxic pollutants derived from natural sources that enter the cultural environment in a planned or desired way (e.g., metals from ore refining) from those which enter in an inadvertent or uncontrolled way (e.g., erosion and runoff) because of the feasibility of establishing control mechanisms for the former.

After anthropogenic sources of the toxic pollutant in the environment are identified and quantified, a comparison of the natural and anthropogenic contributors should be made as to help establish the potential approaches and efficacy of alternative control strategies.

SECTION 5

MATERIALS BALANCE CHECKLIST

As evidenced from the discussion in Section 4, an overall materials balance is comprised of individual balances on a series of industrial and consumer activities, each of which may have various functions, methods, operations, etc. and types of releases associated with them. When performing a materials balance, one must be certain that all potential areas of release have been considered and that each relevant release has been accounted for only once. A materials balance checklist is a convenient approach to assure the accomplishment of these objectives. A materials balance checklist is presented in Figure 22.

The checklist consists of two matrices - a source matrix and an environmental input matrix. The source matrix is comprised of the activities described in Section 4 and various subclassifications appropriate to each activity. Each subclassification indicates items that will form detailed matrices. Thus, an activity with two subclasses containing five and three entries, will result in a total matrix under that activity of a maximum of 15 (5x3) separate items. Each entry in the matrix may not be applicable to every materials balance. As an example, consider a materials balance for a transportation activity in which it has been determined that the material is transported by truck and rail only. All functions and types of release (loading, unloading, routine, accidental, etc.) are relevant to these transportation modes. Using the materials balance checklist, one can develop a detailed materials balance. This procedure will generate a large, but comprehensive, checklist that can help assure consideration of all sources.

The other portion of the materials balance checklist is the environmental input matrix. This matrix is composed of the environmental compartments - air, land and water - and release data - quantity, rate and form. Biota could be used as another compartment. The release data consists of quantities in lb/year or total pounds released, the rate in quantity per time and the form - solid, liquid, or gas. The environmental input matrix can be further expanded to include specific locations or other data relevant to the compartment receiving the toxic pollutant. Again, only certain environmental compartments may be applicable to the situation. By using the materials balance checklist, the person performing the materials balance can develop a detailed output format to assure complete coverage of all activities, environmental compartments and release data.

SOURCE MATRIX			ENVIRONMENTAL INPUT MATRIX *								
			AIR			LAND			WATER		
			Quantity	Rate	Form	Quantity	Rate	Form	Quantity	Rate	Form
EXTRACTION											
Extraction Method	Type of Release										
e.g., drilling dredging strip mining pit mining wastes (to disposal balance)	routine accidental										
REFINING											
Operations	Type of Release										
e.g., washing grinding extraction distillation physical separation wastes (to disposal balance)	routine accidental										
MANUFACTURING											
Manufacturing processes	Material Class	Type of Release									
e.g., chemical reactions cracking digestion wastes (to disposal balance)	contaminant by-products/ co-products primary product	routine accidental									

Figure 22. Materials balance checklist.

			ENVIRONMENTAL INPUT MATRIX								
			AIR			LAND			WATER		
			Quantity	Rate	Form	Quantity	Rate	Form	Quantity	Rate	Form
PROCESSING											
Processes	Material Class	Type of Release									
e.g., extrusion molding calendering drying pressing cutting wastes (to disposal balance)	present in raw material added during processing by-product of processing	routine accidental									
TRANSPORTATION											
Mode	Function	Type of Release									
truck rail vessel air pipeline	loading transit unloading cleaning/ maintenance	routine accidental									
STORAGE											
Methods	Function	Type of Release									
tanks bags piles drums underground misc. containers	loading during storage unloading cleaning/ maintenance	routine accidental									
USE											
Type of Use	Sector	Type of Release									
confined consumptive distributed applied	domestic commercial industrial institutional agricultural	routine accidental									

Figure 22 (Continued)

			ENVIRONMENTAL INPUT MATRIX								
			AIR			LAND			WATER		
			Quantity	Rate	Form	Quantity	Rate	Form	Quantity	Rate	Form
DISPOSAL											
Type of Material	Type of Disposal	Type of Release									
product	POTW	routine									
container	landfill	accidental									
applicator	incineration										
clean-up	ocean dumping										
contact	land farming										
wastes	pre-treatment										
	septic system										
NATURAL SOURCES											
Type	Source/Activity										
historic	resource deposit										
contemporary	soil										
	biota										
	volcanic activity										
	formation in upper atmosphere										
	natural combustion										
	lightning										

Figure 22 (Continued)

	AIR			LAND			WATER		
	Quantity	Rate	Form	Quantity	Rate	Form	Quantity	Rate	Form
TRANSPORTATION									
Truck									
Loading									
Accidental									
Routine									
Transit									
Accidental									
Routine									
Unloading									
Accidental									
Routine									
Cleaning/Maintenance									
Accidental									
Routine									
Rail									
Loading									
Accidental									
Routine									
Transit									
Accidental									
Routine									
Unloading									
Accidental									
Routine									
Cleaning/Maintenance									
Accidental									
Routine									

*Another environmental compartment that can be considered in the environmental input matrix is the biota compartment. Depending upon the specific chemical considered and the scope of the materials balance, biota could be included in loading estimates.

Figure 22 (Continued)

SECTION 6

FEASIBILITY OF MATERIALS BALANCES

INTRODUCTION

One of the goals of this program was to assess the overall feasibility of materials balance methodologies. As explained earlier, a significant number of separate, defined approaches or methodologies for materials balances were not identified in the literature or in current reports. As a result, a composite approach or methodology was developed and described for each major industrial (and consumer) activity associated with the flow of toxic pollutants from their inception to disposal. Because there is only one basic approach to materials balance for each activity, and because each activity can be considered somewhat independent of the others, an assessment or ranking of the feasibility of the methodologies is not appropriate. Furthermore, our experience in conducting materials balances for different chemicals suggests that a materials balance methodology suitable for one chemical or class of chemicals may not be suitable for another chemical or class of chemicals. Expressed in a different way, a materials balance methodology may be feasible but not implementable for all chemicals to the same degree of success.

Nevertheless, it is useful to develop and present a set of requirements and feasibility criteria for materials balances. Users of the materials balance methods described in this report can then make their own feasibility assessments, bearing in mind the purpose and requirements of the materials balance and the particular characteristics of the toxic pollutant, in order to help choose among detailed approaches and considerations in performing the materials balance.

MATERIALS BALANCES DEFINITIONS AND REQUIREMENTS

A materials balance is an array of the flows of materials or chemicals from the cultural environment to the first point of entry into the natural environment with information regarding the location, time, rate, quantity and chemistry of the flows. The materials balance also accounts for redistributions within the cultural environment and, for completeness, must also include the flows resulting from natural sources of materials or chemicals. Materials balances may be described in terms of geographical scale and specific characteristics. Geographical scale refers to the breadth of the boundaries encompassed by the materials balance whether it be global, national, regional or local. Specific characteristics refers to the direction or focus of the materials balance, for example, toward specific industry sectors--manufacturing, disposal, transportation; specific environmental media--air, water, land; specific chemicals or chemical groups; and a specific time frame--current, past, or future. Thus, specification of the geographical scale and the characteristic parameters defines the scope of the materials balance.

Requirements for materials balance data arise from regulatory considerations and from the longer range aspects of research and development activity. Assessments of risk for chemicals appear in several statutory provisions of the U.S. Environmental Protection Agency. This mandate has also been imposed by the courts in some cases. Furthermore, it is implied that exposure and risk assessments become a primary EPA responsibility in the pre-market notification process under the Toxic Substances Control Act. This establishes additional requirements for materials balances.

Two general types of requirements emerge for materials balances under consideration here. One is the application to exposure assessments used for risk analysis and the other is directed toward research and development. The exposure assessment application of materials balances may use either the materials flows for direct determination of exposure or for inputs to transport and transformation (fate) models that are, in turn, used to determine exposure. Examples of direct application are the occurrence of a chemical in a product coming in direct contact with sensitive receptors or the direct emission of a chemical to air which exposed populations breathe. The indirect application to exposure assessment uses estimates of releases of a chemical into an environmental medium and, after subsequent distribution and/or transformation, the chemical is then contacted by some target. Therefore, the intervening step of model calculation spans the gap between release and exposure.

Uses of materials balance other than for full risk analysis information include the development of indices for screening purposes and the accounting of materials flows simply to know more about the principal impact points in environmental compartments. All of these applications may be used in brief studies designed for short-term regulatory applications.

FEASIBILITY CRITERIA

Having defined materials balances and examined their general requirement, we can now focus on criteria for examining the feasibility of a risk assessment methodology.

We have presented the feasibility criteria below in descending order of importance. The rank assignments were made in discussion and evaluation meetings among Arthur D. Little, Inc., staff and EPA staff both for new chemicals and for existing chemicals. The scale chosen was 1 (least important) to 5 (most important). The format of the list is to give the brief title of each criterion followed by a ranking for new chemicals and a ranking for existing chemicals (in parentheses) expressed on the 1 to 5 scale. A question or series of questions will be posed for each criterion to provide further explanation.

- Uncertainty (5,5)* Does the user have a clear indication of the sources and magnitudes of uncertainty levels?

- Human Resources (5,5) How much labor effort is needed to complete the materials balance?

- Time (5,5) How much elapsed time is required to produce the complete materials balance?

- Controllable Sources (4.5, 5) Does the method permit the identification of critical sources that are susceptible to controls?

- Exposure (5,4) Does the end result provide a direct route to the prediction of exposure?

- Comprehensiveness (4.5, 4.5) Does the methodology ensure completeness of coverage of sources of chemical release over the complete range of activities?

- Similarity (4.5, 3) Can other chemicals in similar use categories be used as guides in obtaining predictive values for releases?

- Interface (2.5, 4.5) Does the form of the materials balance output data match the requirements and availability of fate data and models?

- Accuracy (2, 3.5) Are the source mass flows accurate in a quantitative sense?

- Compatibility (1.5, 3.5) Does the method require data that are consistent with the form of existing input data presentations and consistent with descriptions of materials balance control strategy?

- Scale Range (2.5, 2.5) Can global, regional, and local assessment be made using the methodology in question?

- Resolution (1, 3.5) Is there sufficient depth of detail both in spatial and temporal description of materials releases?

- Monitoring Requirements (not available,** 2.5) Are monitoring measurements required to confirm or provide the values in the materials balance?

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*The first number is the index for new chemicals and the second, for existing chemicals.

**In general, monitoring data will not be available for new chemicals.

- Confidentiality (1, unacceptable*) Does the implementation of the methodology require the use of trade secrets or other proprietary information?

- Data Processing Demands (low, low) Are unusual amounts of computer usage required for completing the materials balance?

- Complexity (-, -)** Are the data inputs unacceptably complex?

DISCUSSION

Most of these criteria have been taken into consideration in the development and description of the materials balance methodologies given in Section 4. Here we will discuss major criteria briefly to show their use in evaluating the feasibility of materials balance approaches.

Uncertainty

In order to have a firm basis for regulatory or administrative action, the uncertainties in a materials balance, both in terms of the sources and magnitudes, must be well established. It is not necessary that the uncertainty be reduced to low levels or minimized, since this may require extensive resources, but the materials balance should indicate the degree of uncertainty in the results. For example, one should be able to make statements as a result of a materials balance, such as . . . "80% ± 5% of the chemical enters the natural environment from land disposal of manufacturing waste from the XYZ process; this occurs in locations A, B, C and D. The uncertainty in the estimate results from variations in the composition of the waste . . ." In order to have a clear indication of the sources and magnitudes of uncertainties, (1) a materials balance must be done to a high degree of completion--or at least the releases that represent a high percentage of the total must be accounted for, and (2) the uncertainties occurring in any part or subcalculation, for example, in an extraction or manufacturing step, etc., must be "carried through" the analysis. Therefore, in planning approaches to materials balance, it is usually desirable to focus intially on the major flows reaching the environment, to place in perspective other flows and to reduce uncertainty levels, and thus to proceed with smaller flows which could have important exposure or risk potential. Through using several estimation techniques, or by using measurements or monitoring data, some of the uncertainties in flows can be quantified. Also, independent checks on flows leaving one activity and entering another can help establish and/or reduce uncertainty.

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*Confidential data should not be used for existing chemicals.

**Not expected to be an important criterion.

Human Resources

Depending on the geographic scale, the characteristics, the chemical(s) involved, and the end use(s) of the materials balance, the resources required can vary from several person days to several person years. The materials balance approach must be flexible in its output, and preferably have a high initial return for a small investment in resources. Thus several days of effort should yield quantitative estimates of major flows, with more detail on minor flows, increased accuracy and resolution, resulting from additional effort. This is true for balances associated with new and existing chemicals but for different reasons. Extensive resources will not likely be available for chemicals that are only in the premanufacturing stage. For existing chemicals, it is essential to determine, with limited resources, whether the chemical is a "problem" so as to make most effective use of resources on a large number of chemicals. Those approaches which necessarily require extensive resources--personal interviews, monitoring, site surveys, etc.--should be reserved for later stages of materials balances when it is determined that it is necessary to use these resources to improve accuracy, insure completeness, develop a more certain regulatory base, etc.

Time

As is the case with human resources, the time required for materials balance can be critical in some regulatory programs. Those techniques which provide the most comprehensive data in the shortest time (for example, computerized data base access, use of emission factors where available) should be considered first and those which require extended efforts--questionnaires, surveys, measurements--considered later if warranted.

Controllable Sources

A major function of a materials balance is to help identify sources of toxic pollutants that are amenable to control and points at which controls may be appropriate. A carefully structured materials balance, which describes types, locations, quantities, and rates of release or environmental loadings, together with the form of material during release and the environmental compartment which the material enters can identify possible control points. In conducting a materials balance, it is useful to focus initially on those releases which are concentrated, both in geographic, chemical, or quantity terms, since these may be more controllable than dispersed releases. Identification of transfers from one activity to another also helps suggest control points in a materials balance, for example, from storage to transportation, from manufacture to disposal, etc.

Exposure

The central thrust of many toxic pollutant control strategies is to reduce the exposure of populations to the chemical of concern. A

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materials balance should help in identifying both direct and indirect exposure. This can best be done by consideration of the refining, manufacturing, processing, storage, etc., activities showing releases to the environment that can result in worker exposure, the use and use patterns, transportation activities, and disposal activities that can result in broad public exposure, and the air and water releases that result in exposure of large non-human populations. It is helpful at each step in the materials balance process--or for each environmental release--to ask the question, "Can this release result in significant direct or indirect human or non-human exposure?". Those releases with high exposure potential need to be examined more closely to improve the accuracy, decrease the uncertainty, and to identify control measures.

Comprehensiveness

The materials balance checklist represents a useful tool to help assure the comprehensiveness of a materials balance. It can aid in brief examination of sources or activities that may, at first thought, not be significant, but on further consideration result in considerable exposure potential. This does not imply that all activities and sources must be examined at the same depth but, at least, considered and placed in perspective.

Similarity

In some cases, particularly for new chemicals, there will be insufficient data to conduct a materials balance. For example, there may not be data on releases during production, fugitive losses during storage or transport, or estimates of disposed quantities. In the absence of data, analogies to other similar chemicals should be sought. One should consider using data on chemicals with the same or closely related physical and chemical properties to develop the materials balance for the chemical when no data are available. Chemicals having similar use, transportation or disposal patterns might be examined to set upper and lower bounds of releases to the environment. Of course, it will be necessary to display clearly the assumptions in these estimates, but the approaches can aid when data are lacking.

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Interface and Compatibility

These two criteria are quite similar; the first addresses the output of a materials balance, the second the input. Since one of the goals of a materials balance is to provide inputs to fate, exposure and risk analyses, the output of the materials balance should provide data on concentrations, chemical form, amounts, locations, rates, etc., suitable for fate models or calculations. Thus in developing materials balances, one should attempt to develop ranges of expected environmental loadings for different environmental conditions or scenarios that can be used in fate analyses. Specification of the receiving environmental media will be important for this purpose. The approaches to developing

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materials balances should be compatible with existing data bases used as inputs--for example, SIC classification, census of manufacturers data, STORET data, etc. Compatibility should not be too great a problem; more likely the absence of data in these bases will be the major difficulties.

Accuracy

In order to develop control measures and make accurate predictions of fate, exposure or risk, it is desirable to know the flow quantities and rates of toxic pollutants as accurately as possible. However, the accuracy needed in various parts of a materials balance is relative. If 95% of the flow enters a single compartment from a single type of source, a high accuracy may be required for accurate exposure prediction. If a source represents only a small fraction of the total discharge, great accuracy may not be required. As indicated in the rankings, knowledge of uncertainty in release estimates is more important, in general, than absolute accuracy. Therefore, in conducting materials balances, estimates and professional judgment may often suffice rather than requiring quantitative measurements that are resource intensive.

Scale Range and Resolution

These criteria are also interrelated. On one hand, the materials balance method must be useful in global, national or local estimates, while on the other hand, must have resolution capabilities consistent with the scale. This suggests that global balances will be done with a minimum of detail and low resolution. Methods such as use of emission factors, aggregation at the plant or state level may be feasible. For local balances, consideration of details of each activity and reliance on measurements or monitoring, rather than gross estimates, will be more appropriate. Global scale balances will normally require consideration of longer time frames, while local balances will require shorter time frames for analysis.

Most of the other criteria listed above are of lesser importance and will not significantly affect the choice of materials balance methods or the feasibility of conducting materials balances.

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4. Sargent, D.H. and J.R. Metz. Technical and Microeconomic Analysis of Cadmium and Its Compounds. U.S. Environmental Protection Agency, Report No. 560/3-75-005, March, 1975.

APPENDIX A

ANNOTATED BIBLIOGRAPHY

R.B. Biggs, J.C. Miller, M.J. Oxley and C.L. Shields. A Mass Balance Model of Trace Metals in Several Delaware Watersheds, NTIS PB-266 243/4, November 1973.

This report summarizes sampling work done over several years at various locations in seven Delaware streams. Rainfall and stream samples were analyzed for a variety of metals. Using these data and information from other sources on hydrology and stream flow, the authors utilized the basic materials balance outline of:

input - output + generation - depletion = accumulation.

A.C. Cogley, Large-scale Mass Balance for Lead in Southern Michigan. NTIS PB 232 956, December 1973.

The study addresses the input and output of lead in the Southern Lake Michigan watershed. The primary source is from gasoline, which is in turn related to other (undefined) sources. The final compartment is water.

Lead is conceived to enter three environmental compartments -- air, land and water. The outputs from air and land are losses and inputs to the water environment as well as transfers between the two compartments.

The author utilized transport models reported in the literature coupled with sampling data and gasoline consumption to calculate output quantities. In some cases he used his own judgment on the order of magnitude of certain quantities. Most of the data available are for extended time periods, so an average value is utilized. The main drawback of the materials balance is the inability to represent the dynamic situation that is occurring.

The report recognizes that there are certain processes which exist but about which there is no specific information. The unknown quantities are represented as variables in the materials balance summary in both source and sink values.

Lowenbach and Schlesinger, Arsenic: A Preliminary Materials Balance, EPA Report 560/6-005, March 1979.

The report is basically a summary of literature data and a limited amount of survey information. The report includes natural and anthropogenic sources. The output of the report is a pie chart for each environmental compartment, but no percentage breakdown

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or total numbers are presented. Each segment of the chart, e.g. natural sources, production, smelting, are briefly discussed, followed by a table summarizing the data for inputs and final environmental compartment within the segment.

The methodology itself appears rather straightforward. Natural sources are considered as one category although data are presented for separate processes, e.g. weathering, volcanic activity. The anthropogenic and/or cultural sources are subdivided into production, energy production, various smelting and refining processes, and wastewater treatment processes. The approach consisted of a literature search and then identification of manufacturers and producers. Data from foreign sources are utilized as well as the approach of selecting an analogous chemical on which more information is available and relating it to the chemical of concern. Some survey data on emissions were obtained and some entries were compiled using knowledge of emission factors, process variables, efficiencies, etc.

Stanford Research Institute, Menlo Park, CA., Review of the Environmental Fate of Selected Chemicals, NTIS PB-267 121, May 1977.

This report is basically a literature search. Data for various chemicals are presented on producers, the physical and chemical properties, kinetics, and various chemical transformations. The report is directed towards fate once the chemical is in the environment.

F.L. Rolfe and K.A. Reinbold, Environmental Contamination by Lead and Other Heavy Metals, Vol. I, Introduction and Summary, University of Illinois at Urbana-Champaign, NTIS PB-287 151, July 1977.

This report is a study of the sources, transport, fate and effects of lead and other heavy metals in the environment. The study does present a detailed flow of lead from natural sources through its processing and use to final disposal in the natural environment. The flow diagram, which could serve as a starting point for a materials balance, was drawn up by a group using their own knowledge and experience as the basis. No attempt is made at quantifying flows.

The Mass Balance Equation as Applied to the Distribution of PCBs in the Great Lakes System, Versar, 1976.

The report involves application of the general mass balance concept to explain the wide distribution of PCBs in the environment. The model boundaries are the natural environment. The study develops a model that recognizes possible processes that could occur to account for the fate and transport of PCBs. Available data, both monitoring and literature, are used as inputs to the model or to aid in estimation of necessary values. The model attempts to account for both spatial and temporal distribution and effects. The model is applied to the Great Lakes System.

Mass Balance Determination for Pollutants in Urban Regions: Methodology with Applications to Lead, Zinc, Cadmium, and Arsenic, Dept. of Environmental Health Engineering, California Institute of Technology NTIS PB-286 241, August 1978.

This report summarizes the development of a model to determine the fate of airborne trace-metal pollutants.

Any materials balance requires certain basic types of information. These types are input data, e.g., emission rates, receptor data, e.g., deposition rates, and output, e.g., flow paths.

The first step in the methodology is to define in broad, general terms the pathways and the end points for the chemical of interest. After the broad categories are defined, specific pathways are drawn for each one.

Cal Tech utilizes a vector approach to characterize the model described. Basically, this consists of listing all sink vectors, and all emissions vectors. These are used to generate a source-sink matrix.

After development of the model, they proceeded to locate data for the model. The information came primarily from the literature, experimental work they carried out, discharge permits and eventually, judgment. During the review of literature, they searched for data from different sources that would hopefully substantiate each other. Two approaches were suggested for cases where there was a lack of data. The first was to determine if another chemical existed that either behaved very similarly to the one of concern or could be related to the chemical under study via some ratio and there was sufficient information on it in the literature. The other approach was to fit various pieces of information into a model and/or actually collect data. All this information is then substituted in the appropriate source or sink vector. The vectors are then used to generate the final matrix.

Materials Balance and Technology Assessment of Mercury and its Compounds on National and Regional Bases, URS Research Co., NTIS PB-247 000, October 1975.

This report involves three phases: a materials balance, an assessment of the impact of current and projected process technologies on the future emissions of mercury, and a cost impact analysis of proposed regulations relating to discharges of mercury.

The study presents materials balances for selected regions, based primarily on states, and for the nation. Analyses of selected plants and operations are also presented. The results are presented in tabular form and on maps showing relative concentration ranges within the area of interest.

The initial work involved dividing the sources into three major categories: man-made sources, final disposal and natural sources. Man-made sources were further subdivided into sectors based on mining, manufacturing and processing, final consumption (specified in two ways -- commercial/industrial and personal) and unregulated sources. A final subdivision within these main headings was made by use of SIC codes. Natural sources were also subdivided according to the process involved (i.e., runoff, degassing, etc.).

Usage was divided between manufacturing, commerce and the general population. For usage by the general population, the regional consumption was simply defined as:

$$\text{national consumption} \times \frac{\text{population of region}}{\text{national population}}$$

The multifactor, for use in the commercial sector, is based on the percent of all employees in the region involved in manufacturing, wholesale and retail trade, service industries and the government. The manufacturing employment ratio used in the manufacturing sector, is the percent of employees in manufacturing in the region.

Data for natural sources came primarily from the results of models and some historic data. An emission factor was used to allocate releases to the various environmental compartments. The emission factor is used to calculate the estimated losses as follows:

total mercury in category X fraction available X emission factor.

W.B. Neely, "Material Balance Analysis of Trichlorofluoromethane and Carbon Tetrachloride in the Atmosphere," The Science of the Total Environment, 8, pp. 267-274, 1977.

The author develops a model to predict the movement and concentration of various halocarbons in the atmosphere. Following the model development, he uses data on trichlorofluoromethane to test the model and then applies the model to carbon tetrachloride. The model is composed of a number of compartments across whose boundaries transfers occur. Compartments are geographic (i.e. northern hemisphere, southern hemisphere) and environmental (i.e. ocean, troposphere). Rate constants are used to characterize the entry or exit from each compartment. Data on vapor pressure, solubility and production rates are used to estimate the various transfer coefficients. The model is then solved for the various compartmental concentrations.

A Preliminary Analysis of Nitrous Oxide (N_2O) Including a Materials Balance, In-house EPA Report - 560/6-79-001, January, 1979, C. Richard Cothern, Project Officer.

The basic emphasis of this report prepared by EPA is on identification of sources which result in discharge of nitrous oxides to the environment. The bulk of the information used in the work is from literature sources. The information consists primarily of kinetic and half-life data, models for various chemical and biological processes and some sampling data. The materials balance is arrived at by using sampling data and if necessary, assumptions in conjunction with the appropriate models. Most information is presented as ranges along with an estimate of the most likely value.

The sources identified are primarily natural ones. An estimate is made of current emissions from anthropogenic sources (such as fertilizer use). The materials balance is viewed as a "snapshot in time" that should be used to estimate future emissions and then aid in the evaluation of the impact of various control technologies and other factors.

The report makes the point that the large ranges for source and sink values makes it nearly impossible to determine if major sources or sinks have been overlooked.

F.C. Whitmore, Jr., A Predictive Model for the Estimation of the Environmental Load of a Pollutant - A Draft, Versar, Inc. (no date).

This report presents a general mathematical model for materials balance. The losses dealt with are: production, incidental, transportation, end use product manufacture, and end use product service.

The model defines two types of environmental reservoirs: the general environmental reservoir (GER) and the mobile environment reservoir (MER). The MER is that portion of the GER that is in a form that possesses the potential for exposure to sensitive species. Each succeeding segment of the analysis depends on the previous calculation. The total loss to the environment is simply the summation of the losses from various segments. No attempt is made at allocating the losses to one of the environmental compartments. Injections to the MER are determined by estimating the portion of each loss to the GER that may enter the MER and by use of a fate model.

The equations developed in the model are relatively straightforward from a materials balance point of view. The difference between input and output is assumed to be lost. Each manufacturing use and end product are to be included. The model even incorporates the idea of product life-time to estimate the amount entering the GER due to disposal of products containing the material. The author uses PCB's as an example of the use of the model.

K.J. Yost, W.Bruno, J.E. Christian, F.M. Clikeman, and R.B. Jacko, The Environmental Flow of Cadmium and Other Trace Metals, Purdue University, NTIS PB-229 478, June 1973.

This report is a summary of sampling programs to measure cadmium and other trace metals from various point sources, in food crops, in wildlife and in aquatic environments.

APPENDIX B

INFORMATION SOURCES

General

EPA and other government files
Companies - process descriptions, accident data, location of operations, volumes handled
Equipment manufacturers
Government agencies (federal, state and local) - NPDES, sampling data, manufacturers
Opinion Research Corporation
Departments of Public Works
State Departments of Environmental Quality
U.S. Department of Agriculture
Product manufacturers, processers or fabricators: annual reports, private communications, press release

Abstracts and Searches

Pollution Abstracts
Environmental Abstracts
Engineering Index
NTISearch
Applied Science and Technology Index
Metals Abstracts
Bibliographies from U.S. Bureau of Mines
Chemical Abstracts

Industry and Consumer Associations

American Institute of Mining, Metallurgical and Petroleum Engineers
American Institute of Chemical Engineers
American Society for Metals
Society of Mining Engineers
Chemical Manufacturers Association
National Association of Manufacturers
Synthetic Organic Chemicals Manufacturer's Association
National Ash Association
National Association of Recycling Industries
National Solid Waste Management Association
Environmental Information Center
American Society of Sanitary Engineers

- American Public Works Association
- Water and Wastewater Equipment Manufacturers Association
- American Paper Institute
- American Petroleum Institute
- National Agricultural Chemicals Association
- American Iron and Steel Institute
- American Society of Mechanical Engineers
- National Lime Association
- American Institute of Industrial Engineers
- American Chemical Society
- The Fertilizer Institute
- Association of Home Appliance Manufacturers
- Gas Appliance Manufacturers Association

- Chemical Manufacturers Association
- Glass Packing Institute
- Zinc Institute
- Society of Manufacturing Engineers
- Society of Plastic Engineers
- Environmental Defense Fund
- Natural Resources Defense Council
- Opinion Research Corp.
- National Family Opinion

Periodicals

- Chemical and Petroleum Engineering
- Chemical Engineering (Chemical Engineering Equipment Buyers Guide)
- Chemical Engineering Progress
- Chemical Week
- Engineering and Mining Journal
- Mining Engineer
- Pit and Quarry
- Process Engineering
- Chemical Marketing Reporter
- Coal Age
- Coal Mining and Processing
- American Dyestuff Reporter
- American Paint Journal
- American Paper Industry
- Automotive Engineering
- Beverage Industry
- Chemical and Engineering News
- Chemtech
- Food Engineering
- Food Industry
- Machine Design
- Modern Packaging

Modern Plastics
Oil and Gas Journal
Packaging Design
Plant Engineering
Plastics Engineering
Plastics Technology
Plastics World
Pulp and Paper
Rubber Age
TAPPI
Textile Worls
Agricultural Chemicals
AIChE Journal
Chemical Processing
Chemical and Metallurgical Engineering
Water and Sewage Works
Water and Wastes Digest
Water and Wastes Engineering
Industrial Wastes
Solid Waste Report
Solid Wastes Management
Journal of the Water Pollution Control Federation
Journal of the American Water Works Association
Journal of the Air Pollution Control Association

Books

Census of Manufacturers, U.S. Dept. of Commerce, Washington, D.C.
U.S. Geological Survey Yearbook, U.S.G.S., Washington, D.C.
Mineral Facts and Problems, U.S. Bureau of Mines, Washington, D.C.
SME Mining Engineering Handbook, I.A. Given (ed.), AIME, New York.
Chemical Process Industry, R. Shreve and J. Brink, McGraw-Hill, N.Y.
Unit Operations of Chemical Engineering, W. McCabe and J. Smith, McGraw-Hill, New York.
Metal Bulletin Handbook, R. Packard (ed.), Metal Bulletin Ltd., London.
Metal Statistics, P. Cere (ed.), Fairchild Publications, New York.
Minerals Yearbook, U.S. Dept. of Interior, Bureau of Mines, Washington, D.C.
Mining Engineer's Handbook, R. Peele (ed.), John Wiley and Sons, New York.
Oil and Gas International Yearbook, P. Jenkins (ed.), Business Enterprises, London.
Petroleum Processing Handbook, W.F. Bland and R.L. Davidson (eds.), McGraw-Hill, New York.
Chemical Regulation Reporter, The Bureau of National Affairs, Washington, D.C.

Chemical Engineering Practice, H.W. Cremer and T. Davis (eds.) Butterworths Scientific Publications, London

Moody's Industrial Manual, Moody's Investors Service, New York

Encyclopedia of Chemical Technology, R.E. Kirk and D.F. Ohmer, Interscience Encyclopedia, Inc., New York

The Encyclopedia of Chemistry, C.A. Hampel and G.G. Hawley (eds.), Van Nostrand Reinhold Co., New York

Directory of Chemical Producers, U.S.A., Chemical Information Services, Stanford Research Institute, Menlo Park, CA.

Chemical Sources, U.S.A., Directories Publishing Co., Fleming, N.J.

Manufacturing Processes Dictionary, H.R. Clauser (ed.), Technomic Publishing Co., Westport, CN.

Industrial Product Directory, Cahness Publications, Stamford, CT.

SOCMA Handbook, American Chemical Society, New York

Rare Metals Extraction by Chemical Engineering Techniques, W.D. Jamrock, Pergamon, New York

Jane's World Mining, Jane's Yearbooks, London

Mines Register, New York

Handbook of Non-Ferrous Metallurgy, D.M. Liddele (ed.), McGraw-Hill, New York

Clarke, R.K., J.T. Foley, W.F. Hartman, D.W. Larson. 1976. Severities of Transportation Accidents, Sandia Laboratories Report, SLA-74-001.

Annual Reviews, U.S. Air Carrier Accidents, National Transportation and Safety Board, Bureau of Aviation Safety.

Preliminary Analyses of Aircraft Accident Data. (Annual) U.S. Civil Aviation NTSB Reports.

Accidents of Large Motor Carriers of Property. (Annual) Bureau of Motor Carrier Safety, Federal Highway Administration, U.S. Department of Transportation.

Accident Bulletins and annual Summary and Analyses of Accidents on Railroads in the United States. U.S. Department of Transportation, Federal Railroad Administration, Bureau of Railroad Safety.

AAR-RPI Railroad Tank Car Safety Research and Test Project. A series of Reports 1972-1976.

Solomon, K.A., M. Rubin, and D. Okrent, 1976. On Risks from the Storage of Hazardous Chemicals, University of California, Los Angeles Report UCLA - ENG - 76125, December 1976.